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**Total Copper Analyzer for Rapid *In Situ* Characterization of
Effluent Discharges
SI-0311**

Final Technical Report



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14. ABSTRACT The Total Copper Analyzer (TCA) continuously measures total recoverable copper in real-time at environmentally relevant concentrations. The TCA is a continuous-flow system with in-line acidification and digestion, which measures and reports copper in 5 minutes. The TCA is affected by salinity and room temperature. Once these parameters are set relatively constant, it responds linearly to copper concentration with a dynamic range from 0.5 to 400 µg/L in distilled water (DI), and from 2 to 400 µg/L in artificial seawater (i.e., 3.5% NaCl in DI), with a precision of ±10% at 30 µg/L. The TCA is not affected by up to 50 µg/mL cadmium, manganese or zinc; but, it is affected with a 16% decrease in 5 µg/mL humic acids, 31% decrease in 100 µg/L iron, and is poisoned by 20 µg/mL chromium. Measurements in the dry docks at Puget Sound and Pearl Harbor Naval Shipyards showed a dynamic range from 8 to 80 µg/L, with a precision of ±10% at 30 µg/L. But, response was erratic in effluents from Schofield Barracks Waste Water Treatment Plant.					
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Table of Contents

List of Acronyms	iv
List of Figures	vi
List of Tables	ix
Acknowledgements.....	1
Abstract.....	2
1. Introduction.....	3
1.1 Background.....	3
1.2 Objectives of the Demonstration	4
1.3 Regulatory Drivers.....	5
1.4 Stakeholder/End-User Issues	6
2. Technology Description.....	9
2.1 Technology Development and Application	9
2.2 Previous Testing of Technology	10
2.3 Factors Affecting Cost and Performance.....	11
2.4 Advantages and Limitations of the Technology	12
3. Demonstration Design	13
3.1 Performance Objectives.....	13
3.2 Selecting Test Sites/Facilities	13
3.3 Test Site/Facility History/Characteristics	14
3.4 Present Operations	15
3.5 Pre-Demonstration Testing and Analysis	18
3.5.1 Laboratory Characterization	18
3.5.1.1 Long-term Laboratory Characterization with San Diego Seawater.....	19
3.5.1.2 Long-term Laboratory Characterization with DI.....	21
3.5.1.3 Interference by Metals and Humic Acid.....	24
3.6 Testing and Evaluation Plan	28
3.6.1 Demonstration Set-Up and Start-Up.....	28
3.6.2 Period of Operation.....	28
3.6.3 Amount/Treatment Rate of Material to be Treated.....	29
3.6.4. Residuals Handling	29
3.6.5. Operating Parameters for the Technology	29
3.6.6 Experimental Design.....	30
3.6.7. Demobilization.....	30
3.7 Selection of Analytical/Testing Methods.....	30
3.8 Selection of Analytical/Testing Laboratory.....	31
4. Performance Assessment	32
4.1 Performance Criteria.....	32
4.2 Performance Confirmation Methods.....	33
4.2.1 Demonstration at Puget Sound Naval Shipyard.....	33
4.2.2 Demonstration at Pearl Harbor Naval Shipyard	39

4.2.3 Demonstration at Schofield Barracks Waste Water Treatment Plant.....	43
4.3 Data Analysis, Interpretation and Evaluation	45
5. Cost Assessment	47
5.1 Cost Reporting	47
5.2 Cost Analysis	48
6. Implementation Issues	50
6.1 Environmental Checklist.....	50
6.2 Other Regulatory Issues.....	50
6.3 End-User Issues	50
7. References.....	51
8. Points of Contact.....	52
Appendix A: Analytical Methods Supporting the Experimental Design	54
Appendix B: Data Quality Assurance/Quality Control Plan	55
B.1. Purpose and Scope of the Plan	55
B.2 Quality Assurance Responsibilities.....	55
B.3 Data Quality Parameters.....	55
B.4 Calibration Procedures, Quality Control Checks and Corrective Action.....	55
B.5 Demonstration Procedure.....	56
B.6 Calculation of Data Quality Indicators.....	56
B.7 Performance and System Audits	57
B.8 Quality Assurance Reports.....	57
B.9 ISO 14001	57
B.10 Data Format.....	58
B.11 Data Storage and Archiving Procedures	58
Appendix C: Laboratory Data.....	59
C.1. Total Recoverable Copper measured by Battelle by ICP-MS in discrete samples from PSNS, PHNS and SBWWTP	59
C.2. Total Recoverable Copper measured at SSC-SD by GFAA in discrete samples from PSNS, PHNS and SBWWTP. Total Recoverable Iron measured at SSC-SD by GFAA in discrete samples from SBWWTP.	64
Appendix D: Cost Assessment Data	69
D.1.1 Estimation of commercial analysis of discrete samples for total recoverable copper measurement for a ten years period (Table 13).	69
D.1.2 Estimation of TCA operational costs for a ten years working period (Table 14).	70

List of Acronyms

$\times 10^6$	Million
$\mu\text{g L}^{-1}$	Micrograms per liter, same as parts per billion (ppb)
$\mu\text{g mL}^{-1}$	Micrograms per milliliter, same as part per million (ppm)
μm	Micrometer, or one millionth of a meter
AERTA	U.S. Army Environmental Requirements and Technology Assessments program
BOD	Biochemical Oxygen Demand
BMP	Best Management Practices
CCC	Criterion Continuous Concentration, also referred to as chronic value
CMC	Criterion Maximum Concentration also referred to as acute value
CRADA	Cooperative Research and Development Agreement
Cu	Chemical symbol for copper
Cu-ISE	Copper Ion-Selective Electrode
$\text{Cu(II)}_{\text{aq}}$	Aqueous free copper ion
DoD	Department of Defense
ECAM	Environmental Cost Analysis Methodology
gal day^{-1}	Gallons per day
GFAA	Graphite Furnace Atomic Absorption
HSDH	Hawaii State Department of Health
ICP-MS	Inductively Coupled Plasma with detection by Mass Spectrometry
DI	Deionized Water
IMF	Intermediate Maintenance Facility
mV	Millivolt, one thousandth of a volt
mg L^{-1}	Milligrams per liter, same as parts per million
NaCl	Sodium chloride
NAVFAC	Naval Facilities Engineering Command
NDCEE	National Defense Center for Environmental Excellence
NOV	Notice of Violation
NPDES	National Pollutant Discharge Elimination System
O&G	Oil and Grease
ONR	Office of Naval Research
PHNS	Pearl Harbor Naval Shipyard
ppb	Parts per billion, same as $\mu\text{g L}^{-1}$
ppm	Part per million, same as $\mu\text{g mL}^{-1}$
PAA	U.S. Navy Pollution Abatement Ashore program (also known as 0817 program)
PSNS	Puget Sound Naval Shipyard
QA	Quality Assurance
QA/QC	Quality Assurance/Quality Control
r	Correlation coefficient
SBWWTP	Schofield Barracks Waste Water Treatment Plant
SRM	Standard Reference Material
SSC-SD	Space and Naval Warfare Systems Center, San Diego
SW	Sea Water

TCA	Total Copper Analyzer
T°C	Temperature in degree Celsius
TSS	Total Suspended Solids
U.S. EPA	United States Environmental Protection Agency
WQC	Water Quality Criteria

List of Figures

Figure 1 The Total Copper Analyzer (TCA) is the first instrument capable of measuring total recoverable copper in effluents, <i>in situ</i> , in near real-time, and at environmentally relevant concentrations.	4
Figure 2 Schematic representations of the processes within the TCA for total copper measurement.	9
Figure 3 Calibration curves of the potential (mV) measured with the Jalpaite Cu-ISE in a prototype TCA and the total copper concentration measured by GFAA.	11
Figure 4 Comparison of copper concentrations measured with the TCA with those measured by GFAA in a suite of mixtures of seawater and freshwater under laboratory conditions. The filled red circles are data not used for the regression. The green dashed line indicated the optimal response of 1:1.	11
Figure 5 Diagram of drainage systems in a dry dock at PSNS.	15
Figure 6 Total recoverable copper concentrations ($\mu\text{g L}^{-1}$) measured in a discharge from dry dock 6 at PSNS.	16
Figure 7 Total recoverable copper concentrations ($\mu\text{g L}^{-1}$) measured in discrete samples from discharge B of dry dock 2 at PHNS.	16
Figure 8 Diagram of the treatment process at SBWWTP. The TCA will be demonstrated in the effluent flow after the final sand filtration and prior to chlorination.	17
Figure 9 Physical and chemical characteristics of the effluent at the SBWWTP: TSS; $\mu\text{g mL}^{-1}$, O&G ($\mu\text{g mL}^{-1}$), pH, temperature ($^{\circ}\text{C}$), and flow ($1 \times 10^6 \text{ gal day}^{-1}$).	18
Figure 10 Response of the TCA to seawater from San Diego Bay. The response is represented as the potential (mV) measured by the Cu-ISE. The complex pattern seems to follow both temperature and tidal effects.	19
Figure 11 Effect of salinity (i.e., conductivity) on the response of the Cu-ISE. The TCA was fed with mixtures of seawater from San Diego Bay and deionized water in order to model the salinity of the water. Salinities are given at the top of the figure.	20
Figure 12 Baseline Cu-ISE potential (mV) observed at background concentrations (i.e., less than one $\mu\text{g L}^{-1}$) throughout a long-term laboratory characterization experiment with the TCA in waters of San Diego Bay at different salinities. Salinities are given for each of the observed potentials.	20
Figure 13 Response of the Cu-ISE to changes in temperature at constant salinity and copper concentration. These are regressions of the data for the corresponding range of temperature at specific salinity.	21
Figure 14 Response of the TCA in DI. The response was evaluated as the potential (mV) measured by the Cu-ISE. The data includes multiple injections of single copper concentrations, and multiple automatic calibrations used for the characterization of the TCA.	22
Figure 15 Dynamic range of the TCA in DI. The TCA had a linear response from a log of copper concentration of -8.1 ($0.5 \mu\text{g L}^{-1}$) to -5.2 ($400 \mu\text{g L}^{-1}$).	23
Figure 16 Dynamic range of the TCA in artificial seawater (i.e., DI with 3.2% NaCl, salinity 32). The TCA had a linear response from a log of copper concentration of -7.5 ($2 \mu\text{g L}^{-1}$) to -5.2 ($400 \mu\text{g L}^{-1}$).	23

Figure 17 Automatic spiking of $30 \mu\text{g L}^{-1}$ copper for 45 minutes, when the TCA is equipped with $\frac{1}{8}$ " ID Teflon [®] tubing. The lapse interval to reach this concentration was 25 minutes, with 5 minutes needed to reach baseline concentration at the end of the spiking. Measured on 25 March 2005 during the characterization with deionized water.....	24
Figure 18 No effect on the response of the TCA's Cu-ISE was observed to additions of Mn (top plot), Zn (middle plot) and Cd (bottom plot). The solution matrix is $25 \mu\text{g L}^{-1}$ copper in artificial seawater (DI with 3.5% NaCl, salinity 35) at pH 2. The injected quantities of Mn, Zn, and Cd were 12.5, 25.0, 37.5, and $50.0 \mu\text{g mL}^{-1}$	25
Figure 19 Effect of 10 and $17.5 \mu\text{g mL}^{-1}$ Fe addition on the Cu-ISE response, in DI with 3.5% NaCl (salinity 35), with $25 \mu\text{g L}^{-1}$ copper and pH 2.....	26
Figure 20 Effect of $20 \mu\text{g mL}^{-1}$ Cr (VI) on the response of the Cu-ISE in DI with 3.5% NaCl (salinity 35), with $25 \mu\text{g L}^{-1}$ copper and pH 2.	26
Figure 21 Effect of humic acids (i.e., organic matter) on the sensitivity of the TCA. The matrix is DI at pH 2. The sensitivity is measured as a change in slope for Cu calibrations (10, 20, 30, and $40 \mu\text{g L}^{-1}$ Cu) at each humic acid concentration. A 16% decrease in the response was observed at $5 \mu\text{g mL}^{-1}$ humic acids.....	27
Figure 22 Gantt chart for dates of demonstrations of TCA at PSNS, PHNS and SBWWTP.....	29
Figure 23 Potential (mV) observed for the Cu-ISE throughout the demonstration at PSNS. The potential in light blue color is uncorrected, and the potential in dark blue color is corrected for both conductivity and for the baseline change due to the malfunction of the sample pump. For clarity the y-axis for the corrected Cu-ISE is offset by 25 mV.....	35
Figure 24 Total recoverable copper concentrations ($\mu\text{g L}^{-1}$) at PSNS measured <i>in situ</i> with the TCA and in discrete samples at SSC-SD and at Battelle Marine Sciences Laboratory. The data is from dry dock 6 and is presented as sampling sequence for clarity.....	36
Figure 25 Total recoverable copper concentrations ($\mu\text{g L}^{-1}$) measured by the TCA during the demonstration at dry dock 6 of the PSNS.....	37
Figure 26 Automatic spiking of $20 \mu\text{g L}^{-1}$ copper, indicating a mean increase in total copper concentration of $19.7 \mu\text{g L}^{-1}$, from a mean baseline concentration of $4.70 \pm 0.89 \mu\text{g L}^{-1}$ (average \pm standard deviation), to a mean spiked concentration of $24.4 \pm 0.90 \mu\text{g L}^{-1}$. The lapse interval to reach this concentration was 11 minutes, with 9 minutes needed to reach baseline concentration at the end of the spiking. Measured on 26 July 2003 at PSNS.	39
Figure 27 Total recoverable copper concentrations ($\mu\text{g L}^{-1}$) at PHNS measured <i>in situ</i> with the TCA and in discrete samples at SSC-SD and at Battelle Marine Sciences Laboratory. The data is from dry dock 2 and is presented as sampling sequence for clarity. TCA sampling stopped during the third week (blocked sampling tube) resulting in no samples taken for sample sequences 10 through 18.....	40
Figure 28 Total recoverable copper and automatic copper spiking of the effluent at dry dock 2 in PHNS.	40
Figure 29 Response of the TCA to pumping in dry dock 2 at PHNS. An increase in total recoverable copper was observed every time the pump was activated, and a subsequent decrease is observed once the pump is deactivated.	43
Figure 30 Total recoverable copper, automatic copper spiking measured at the effluent and temperature in the TCA system at SBWWTP.	44

Figure 31 Total recoverable copper and iron concentrations ($\mu\text{g L}^{-1}$) at SBWWTP. Copper was measured *in situ* with the TCA and in discrete samples at SSC-SD and at Battelle Marine Sciences Laboratory. Iron was measured in discrete samples at SSC-SD. The data is presented as sampling sequence for clarity..... 45

List of Tables

Table 1 Characteristics of effluents from the dry docks at PSNS and PHNS, and of the treated effluent at SBWWTP.	7
Table 2 Performance objectives for the demonstration of the TCA in industrial situations at PSNS, PHNS, and SBWWTP.	13
Table 3 Average and one standard deviation for the concentrations estimated for 15 automatic calibrations in deionized water.	22
Table 4 Decrease in the Cu-ISE potential observed for calibration curves made in artificial seawater (3.2% NaCl in DI at pH 2, salinity 32) with different Fe concentrations.	27
Table 5 Performance criteria.	32
Table 6 Performance criteria and confirmation methods for the demonstration of the TCA.	34
Table 7 Comparison of the total recoverable copper concentrations ($[\text{Cu}] \mu\text{g L}^{-1}$) measured in grab samples from PSNS at Battelle and SSC-SD, with those measured in real time, <i>in situ</i> by the TCA. The differences are given by subtracting the measured value from that of the TCA.	37
Table 8 Average, one standard deviation and precision of the increases of concentration measured for automatic calibrations at PSNS.	38
Table 9 Comparison of the total recoverable copper concentrations ($[\text{Cu}] \mu\text{g L}^{-1}$) measured in grab samples from PHNS at Battelle and SSC-SD, with those measured in real time, <i>in situ</i> by the TCA. The differences are given by subtracting the measured value from that from the TCA. “NA” is not available. Statistics are for that data with corresponding TCA data only.	41
Table 10 Average, one standard deviation and precision of the increases of concentration measured for automatic calibrations at PHNS.	42
Table 11 Comparison of the total recoverable copper concentrations ($[\text{Cu}] \mu\text{g L}^{-1}$) measured in grab samples from SBWWTP at Battelle and SSC-SD, with those measured in real time, <i>in situ</i> by the TCA. The differences are given by subtracting the measured value from that from the TCA.	44
Table 12 Average, one standard deviation and precision of the increases of concentration measured for automatic calibrations at SBWWTP.	45
Table 13 Costs for commercial analysis of discrete samples for total recoverable copper over 10 years at a rate of one sample per day. Costs are in thousands of U.S. dollars.	47
Table 14 Costs associated with the use of the TCA over a 10 year life span. Costs are in thousands of U.S. dollars.	48

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Abstract

The Total Copper Analyzer (TCA) for rapid *in situ* characterization of effluent discharges is the first instrument capable of continuous real-time measurement of total recoverable copper at environmentally relevant concentrations. Copper is a priority pollutant and regulatory programs require measurement of total recoverable copper. The TCA is a continuous-flow system that includes in-line acidification, digestion, and measurement of copper with a specialized jalpaite copper ion-selective electrode (Cu-ISE). The preprocessed sensor data is provided to an integrated computer system, for calculation and reporting of total recoverable copper with custom software. The continuous measurement of copper takes less than 5 minutes for completion. The use of the TCA should lead to the elimination of discharge exceedances and Notices of Violation (NOV), it should also allow for accurate calculations of Total Maximum Daily Loads (TMDL), and decreases in cost of effluent management, as the volume of treated effluent can be minimized.

The demonstration of the TCA included laboratory characterization as well as long-term testing under industrial conditions. Laboratory conditions were used for evaluation of the dynamic range, precision, and interference by metals and humic acids. The response of the Cu-ISE is affected by the salinity (i.e., conductivity) of the water, and by the ambient temperature; however, once these parameters are controlled and kept relatively constant, the TCA responds linearly to copper concentration in the effluent. The TCA has a dynamic range from 0.5 to 400 micrograms per liter ($\mu\text{g L}^{-1}$; parts per billion, ppb) in deionized water (DI), and from 2 to 400 $\mu\text{g L}^{-1}$ in artificial seawater [i.e., 3.5% sodium chloride (NaCl) in DI] with a precision of $\pm 10\%$ at 30 $\mu\text{g L}^{-1}$. The response from the Cu-ISE is not affected by up to 50 micrograms per milliliter ($\mu\text{g mL}^{-1}$; parts per million, ppm) manganese or zinc or by up to 30 $\mu\text{g mL}^{-1}$ cadmium, but, is affected with a 16% decrease in sensitivity by 5 $\mu\text{g mL}^{-1}$ humic acids (organic matter), a 31% decrease in sensitivity by 100 $\mu\text{g L}^{-1}$ iron, and it is poisoned by 20 $\mu\text{g mL}^{-1}$ chromium VI.

Demonstration of the TCA under industrial conditions was done in effluent discharges from the dry docks at Puget Sound and Pearl Harbor Naval Shipyards (PSNS and PHNS, respectively), and at the Schofield Barracks Waste Water Treatment Plant (SBWWTP). The range of concentrations in the effluents from the dry docks proved a dynamic range of 5 to 80 $\mu\text{g L}^{-1}$ with a precision better than $\pm 10\%$ at the 30 $\mu\text{g L}^{-1}$ level. Response of the TCA at SBWWTP was affected by the complexity of the effluent matrix. The TCA was able to detect changes in total recoverable copper in the effluent due to operational processes at the dry docks, as illustrated by increases in copper due to quitting of Process Water Collection System at PHNS, or particle resuspension when pumping at PHNS. The TCA has a requirement of daily assessment and inspection in order to correct any obvious problem affecting its response including replacement of reagents, which is required every two to three weeks. Operational costs for the TCA are calculated to be about \$198,000 assuming a ten-year working life. Costs for the current approach of discrete samples and off-site analysis are calculated to be about \$334,000 for the same ten-year period. Besides decreasing the costs for the measurement of the total recoverable copper concentrations, the TCA benefits the manager by providing a continuous measurement of these concentrations, almost in real-time, which can be used for management of the industrial process, and for optimization of regulation and/or treatment of the effluent.

1. Introduction

1.1 Background

Copper is a high-profile ubiquitous contaminant, found in numerous point and non-point source effluents, including those generated by activities from the Department of Defense (DoD). Because copper is highly toxic to larval organisms, the U.S. Environmental Protection Agency (U.S. EPA) considers this heavy metal a priority pollutant, and its discharge is under regulatory control (U.S. EPA, 1980, 1985). Water quality criteria (WQC) for dissolved copper in receiving bodies of water includes a freshwater criterion maximum concentration (CMC), also known as acute value, of $13 \mu\text{g L}^{-1}$ (micrograms per liter or parts per-billion, ppb), a freshwater criterion continuous concentration (CCC), also referred to as chronic value, of $9 \mu\text{g L}^{-1}$. For saltwater those criteria are a CMC of $4.8 \mu\text{g L}^{-1}$ and a CCC of $3.1 \mu\text{g L}^{-1}$ (U.S. EPA, 2003). While concentrations in ambient waters are regulated as the dissolved fraction (i.e., filtered through 0.45 micrometer [μm] pore-size), regulation of effluents is done on the total recoverable fraction (i.e., unfiltered, acidified to pH >2 and digested).

Regulation of discharge of copper in DoD effluents is done on the total recoverable fraction, at the few tens of $\mu\text{g L}^{-1}$ level. Effluent regulation in U.S. Navy dry docks is implemented through National Pollutant Discharge Elimination System (NPDES) permits. These permits typically allow the discharge of effluents with concentrations in the range of the low twenties to the low thirties $\mu\text{g L}^{-1}$ total recoverable copper, as evidenced by the NPDES permits issued to Pearl Harbor Naval Shipyard (PHNS) and Puget Sound Naval Shipyard (PSNS). An interim NPDES permit issued by the Hawaii State Department of Health (HSDH) to PHNS allows a discharge limit of $23 \mu\text{g L}^{-1}$, and an NPDES permit at PSNS allows a daily maximum limit of $33 \mu\text{g L}^{-1}$, with a monthly average of $19 \mu\text{g L}^{-1}$ total recoverable copper. However, it is likely that these regulatory levels will be lowered in the future. The effluent at Schofield Barracks Waste Water Treatment Plant (SBWWTP), which serves the U.S. Army installation in Wahiawa, Hawaii, is also regulated by a NPDES permit for reuse of the processed water. Although this permit does not include copper monitoring, grass root environmental organizations have been concerned with respect to its copper loading (Environment Hawaii, 1991).

Monitoring and treatment of the effluents are needed in order to comply with permit requirements. Once the concentration in the effluent exceeds the permitted values, the effluent should not be discharged to the environment, but diverted for treatment. For example, most fixed U.S. Naval dry docks are equipped with storm and process water collection systems to control the discharge of water generated from the shipyard (Putnam, 1999). Depending on guidelines set by the regulatory permits, the collection system either discharges the wastewater directly into the surrounding marine environment or diverts it to a treatment system. A rapid characterization of the effluent is needed in order to optimize both the management of the effluents, and the operational costs of the installation. However, as the traditional approach for the evaluation of total recoverable copper includes the collection and measurement in discrete samples of the effluent, an expensive process that takes several weeks; there is a need for a real-time-continuous measurement of total recoverable copper, which has not been available, until now.

A rapid, in-place, characterization of total recoverable copper in effluents can be accomplished by the Total Copper Analyzer (TCA) developed under the Navy's Naval Facilities Engineering Command (NAVFAC) Pollution Abatement Ashore Program (Figure 1). This will allow for the rapid separation of the effluent between that in compliance with regulation and that in need of treatment, thus reducing the costs of operation, since the volume of water sent for treatment can be minimized. This characterization will also provide important information for the management of sources of copper within the installation.

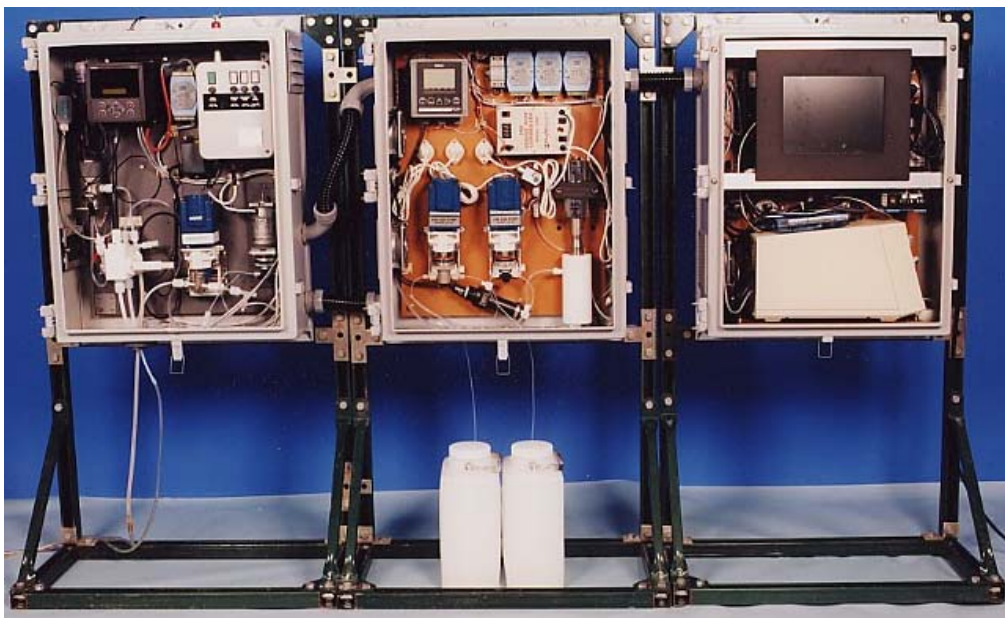


Figure 1 The Total Copper Analyzer (TCA) is the first instrument capable of measuring total recoverable copper in effluents, *in situ*, in near real-time, and at environmentally relevant concentrations.

The demonstration and validation of the TCA is important because there is no other known instrument capable of measuring total recoverable copper, either *in situ* or at real-time. Conventional characterization of the effluent is performed off-site with laboratory tests, is expensive and slow, often taking weeks for processing. As the TCA will provide a means to verify that the discharge is within permit requirements for copper, in real-time, and at the place of discharge, it will be a great asset for any discharger under regulation, both private and public, including the DoD.

1.2 Objectives of the Demonstration

The main objective of the demonstration is to validate the use of the TCA for continuous measurement of total recoverable copper in industrial situations at full-scale. The TCA was deployed in three industrial settings, and was allowed to operate continuously for more than a month in each case. This was done in order to evaluate the maximum lapse of time between maintenance intervals, as the TCA was designed for a 30-day maintenance period, thus the demonstrations were conducted over a minimum of 30 days to validate this performance factor.

These industrial situations also provided the opportunity to evaluate other environmental factors that affected the response of the TCA, namely the operation temperature range and the effect of different matrices (i.e., salinities) in the effluent. This demonstration also compared and validated the concentrations of total recoverable copper measured *in situ* under real-world industrial situations and at near real-time with the TCA, with those measured in discrete samples under laboratory conditions at a private laboratory (i.e., Battelle Marine Sciences Laboratory, Battelle) and at a government laboratory facility (Space and Naval Warfare Systems Center San Diego, SSC-SD). The measurements by the TCA are compared to analytical techniques commonly used for the measurement of total recoverable copper concentrations, namely inductively coupled plasma with detection with mass spectrometer (ICP-MS) and graphite furnace atomic absorption (GFAA).

Three different sites were selected for the demonstration of the TCA in real-world industrial settings. These sites are the saltwater effluent discharges from the dry docks at PSNS, and at PHNS, and the freshwater effluent discharge (prior to chlorination) at the SBWWTP. As with any shipyard, effluents from the dry docks at PSNS and PHNS are derived from the processes for vessel's surface preparation, metal plating and surface finishing, welding and metal cut, machining and working, solvent cleaning and degreasing, and vessel cleaning operations (Kura and Tadimalla, 1999). The effluent at SBWWTP is treated municipal wastewater (freshwater) that is used for irrigation of agricultural fields; it is piped from the SBWWTP into an irrigation flume at the outlet of nearby Lake Wilson, from where it is diverted for use downstream. The specific characteristics for the three effluents are presented in Table 1.

An additional objective resulted from the demonstration at PSNS, which was the first place for demonstrating the TCA. From the results of this demonstration it was decided to modify the plumbing system in the TCA by reducing the outside diameter of the tubing used from 1/4" to 1/8", in order to decrease the detection time of the system. Therefore, an additional objective was the quantification of the performance improvement resulting from the use of the smaller tubing system.

Validation of the TCA was also done under laboratory conditions. The response of the TCA to a large range of concentrations (dynamic range), the precision and accuracy of its measurements, and the effect of possible interferents was evaluated in laboratory-controlled settings at SSC-SD. These laboratory conditions are required in order to isolate and measure this set of parameters.

1.3 Regulatory Drivers

Federal regulations that require the determination of total recoverable copper concentration in effluents include the WQC (U.S. EPA, 2003), and the NPDES program which was developed under the Clean Water Act (CWA) to eliminate or reduce pollutant inputs to aquatic systems by imposing concentration limitations on discharges.

DoD drivers for the measurement of total recoverable copper concentration, *in situ* and in real-time include the following environmental requirements from the U.S. Navy Pollution Abatement Ashore (PAA) program (http://www.paa.navy.mil/PAAEnvironmentalRqmnts_Archive.aspx), and the U.S. Army Environmental Requirements and Technology Assessments (AERTA; <https://www.denix.osd.mil/denix/DOD/Policy/Army/AERTA/tncstop.html>):

- (2.II.2.b)** Improved field analytical sensors, toxicity assays, methods, and protocols to supplement traditional sampling and laboratory analysis.
- (2.II.1.k)** Control/Treat Nonpoint Source Discharge.
- (2.II.2.c)** Nonpoint source discharge identification (local and remote).
- (2.II.1.q)** Control/Treat Industrial Wastewater Discharges.
- A(2.2.f)** Develop New Technologies for Treatment, Monitoring, and Quality Control/Quality Assurance of Army Wastewaters

1.4 Stakeholder/End-User Issues

The primary objective of this demonstration is to prove to the stakeholders the qualifications of the TCA. Parameters determined in the demonstration include the precision and accuracy of the total recoverable copper measurements by the TCA, the dynamic range of these measurements, the working-life expectancy of the instrument, and the required maintenance schedule. Results from this demonstration are provided to stakeholders for any decision concerning the TCA.

The TCA is designed for continuous measurement of total recoverable copper in industrial discharges. The community targeted by the TCA includes complex industrial settings, with requirements on the copper discharge loading. These include DoD supported industrial operations such as those in dry docks and wastewater treatment plants. In general, copper discharge from these industrial operations is regulated as total copper concentration and normal operations in these industrial settings call for equipment for these measurements that it is easy-to-use and requires minimum-maintenance. These requisites and requests are intrinsically included in the performance/acceptance criteria of the TCA, as it allows for total copper measurements at environmentally relevant concentrations, and is a user-friendly instrument with minimal maintenance.

There are two results from this demonstration that have great influence in the implementation and use of the TCA. First, the TCA requires daily inspection, to this point there are not alarms set in the instrument to indicate malfunctioning, and erroneous concentrations could be measured if the system is not functioning correctly. These erroneous measurements were observed in cases where there were problems with the pumping systems in the TCA. The second factor is that ambient temperature can have a strong effect in the measurements done by the TCA. At PSNS and PHNS the TCA was deployed under very constant room temperature conditions and the measurements were fairly stable, being affected only by real changes in copper, evidenced by comparison with the discrete sampling effort/analysis. This is in contrast to the temperature conditions at SBWWTP, where the TCA was deployed in a plastic hut on open grounds. The daily range in temperature within the hut affected the measurements of total copper by the TCA, giving a large range in concentrations (3.5 to 33.2 $\mu\text{g L}^{-1}$), in comparison to the fairly constant concentrations measured in the discrete samples (Battelle: average $5.19 \pm 0.43 \mu\text{g L}^{-1}$, range 4.32 to 6.06 $\mu\text{g L}^{-1}$; SSC-SD: average $4.4 \pm 0.6 \mu\text{g L}^{-1}$, range 3.4 to 5.6 $\mu\text{g L}^{-1}$; Table 9). Therefore, in order to optimize the performance of the TCA, it should be installed in a situation where the temperature is held fairly constant.

Table 1 Characteristics of effluents from the dry docks at PSNS and PHNS, and of the treated effluent at SBWWTP.¹

Parameter	Outflow	Salinity	Biochemical Oxygen Demand	Chemical Oxygen Demand	Total Organic Carbon	Total Suspended Solids	Oil and Grease	pH	Temperature	Ammonia as Nitrogen	Total Nitrogen	Total Phosphorous
Symbol			BOD	COD	TOC	TSS	O&G	pH	T°C			
Units	gal day ⁻¹		mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹		°C	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹
PSNS One sample event												
	0.6×10 ⁶	32	<5	760	6.2	11	<5	7.6	11.5 to 13.2	0.69		
PHNS Measured from May 1996 through June 2003 (n = 77) at one of the two discharges (2B) at dry-dock 2 (DRY DOCK 2)												
Mean value		33	2.2	205		11	0.7	8	1.1	0.068	0.332	0.038
One Standard Deviation			0.4			4	0.4	0.2	0.9	0.107	0.230	0.062
SBWWTP Between January 2003 and June 2004												
Mean value	2.06×10 ⁶	0	1.5			4.5	4.3	6.7	26.8		3.1	3.3
One Standard Deviation	0.26×10 ⁶	0	1.0			4.5	9.0	0.3	1.2		4.6	1.7

¹ The salinities reported here are those measured in the actual demonstrations of the TCA for those effluents.

The use of the TCA as a regulatory tool is not intended as part of this demonstration. The TCA was designed as a management tool for complex industrial effluents, and the objective of this demonstration was to validate this. The TCA is not intended for the replacement of periodical monitoring of the discharges. However, the capabilities of the TCA will be made available to regulators, and to the public, by means of relevant conferences, and appropriate DoD information centers for its possible consideration for regulatory use. The TCA will be produced and commercialized by Thermo-Orion, Inc., and will be available to the public in general.

2. Technology Description

2.1 Technology Development and Application

The TCA is designed to accomplish in real-time Method 3020A, approved by the U.S. EPA for “Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy” (U.S. EPA, 1992). In order to accomplish this goal, the TCA includes in-line automatic acidification, fast digestion of the effluent with an ultrasonic probe, and the use of a specialized jalpaite copper ion-selective electrode (Cu-ISE), instead of GFAA, to measure the concentration of copper. Due to the characteristics of the acidified and digested effluent, a substantial amount of the copper is present as aqueous free copper ions ($\text{Cu(II)}_{\text{aq}}$), which are detected by the Cu-ISE, and the resulting measurement is equivalent to the total recoverable copper concentration.

The analysis consists of three processes, a chemical/physical treatment (i.e., acidification to pH 2 and digestion) of the sample, detection and reporting, and neutralization prior to discharging (Figure 2). In order to reduce contamination and to extend the working life of the TCA, most of the parts of the TCA that are in contact with the effluent are made of Teflon[®]. A continuous stream of effluent is pumped into the TCA at a constant rate (13.8 mL min^{-1}), which is first treated chemically by acidification to pH 2 with 5% nitric acid (0.25 mL min^{-1}) and then physically digested by ultrasonification. The digestate is then directed to the detection system, which includes a conductivity probe, air pump, working and reference electrodes, and a pH electrode. The working Cu-ISE and the high-volume single-junction reference electrode measure a potential (millivolt, mV) that is equivalent to the concentration of $\text{Cu(II)}_{\text{aq}}$. This potential, as well as temperature, pH and conductivity are fed into a computer for the calculation and reporting of the total concentration of copper in the effluent. Finally, the sample is neutralized to pH 7 with 6% sodium bicarbonate (0.55 mL min^{-1}) before it leaves the TCA.

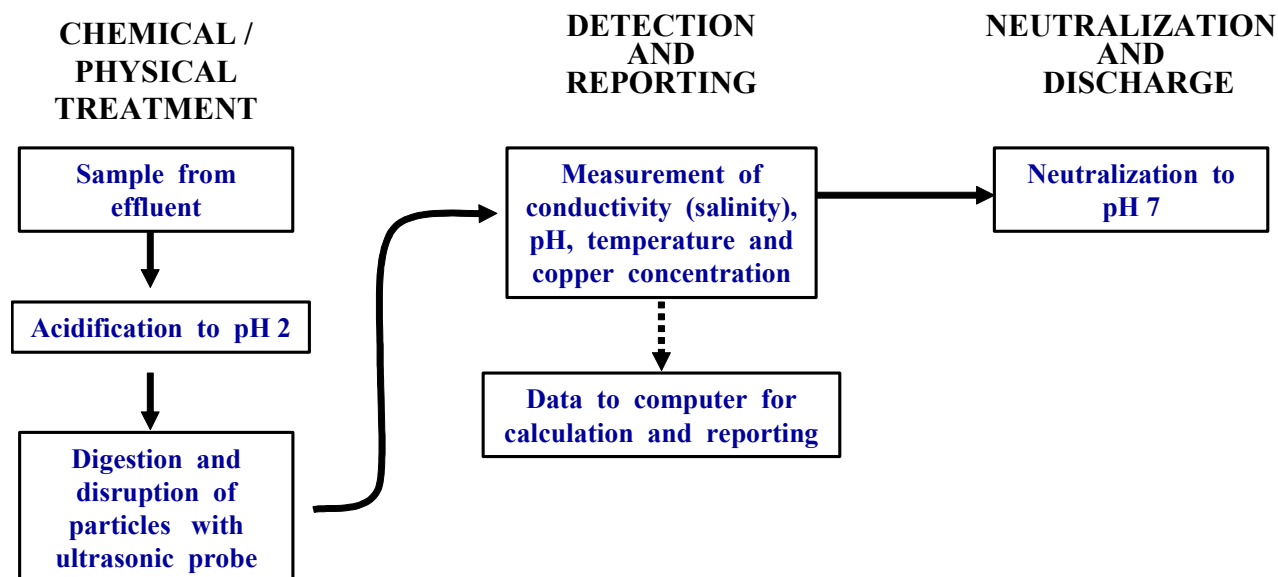


Figure 2 Schematic representations of the processes within the TCA for total copper measurement.

The use of the Cu-ISE for $\text{Cu(II)}_{\text{aq}}$ measurements was initially supported by the Harbor Processes Program of the Office of Naval Research (ONR). The effort was a general development of electrochemical sensors for real-time measurements in marine environments. The results of the ONR project were directed at the project “Real-time Monitoring of Copper from Effluent Discharges,” funded by the NAVFAC Pollution Abatement Ashore program, 0817, which supports 6.4-type (demonstration) research. A product of this project was the creation of a Cooperative Research and Development Agreement (CRADA) with Thermo-Orion, Inc., the world’s largest producer of electrochemical sensors and instrumentation. This CRADA promoted the collaboration with the Research and Development Department of Thermo-Orion, for development of the TCA. This CRADA will also promote the commercial manufacturing of the TCA by Thermo-Orion, Inc.

The TCA has the potential for adaptation for the measurement of total dissolved copper or free copper ion in the effluent. The main difference between total recoverable and dissolved recoverable copper is the filtration of the effluent before its acidification. This filtration process could easily be adapted into the TCA by placing a filtering system before the acidification of the sample. Once the effluent is filtered, the measurement of copper in the effluent would be identical for both total recoverable and dissolved copper. However, as effluent discharge is regulated as the total recoverable copper, setting up the TCA for dissolved copper measurements was not studied in this demonstration. Similarly, free copper ion is not regulated at this time; therefore this kind of measurement was not included in this effort. Nevertheless, the TCA could be easily adapted for the measurement of free copper ion in the effluent, or in the receiving body of water. Concentration of free copper ion is dependent on ligands, suspended solids, pH, ionic strength (salinity), temperature and other chemical and biological parameters in the water. As the content and characteristics of these parameters is affected by acidification and digestion, avoiding these processes will provide the Cu-ISE with the real matrix for the measurement of free copper ion. The TCA is capable of being modified for this purpose however; a simpler system should be able to provide the same measurement.

2.2 Previous Testing of Technology

A prototype TCA in the final phase of development was tested under laboratory conditions at SSC-SD before starting the demonstrations. This testing was done in laboratory-controlled conditions with mixtures of seawater and freshwater of known total copper concentrations, in order to create calibration curves for the instrument. The calibration curves are most noticeably affected by salinity. However, the slope of the curves remained essentially constant (Figure 3). Therefore, it is necessary to measure the salinity of the effluent in order to select the most appropriate calibration curve. Since there is a direct relationship between salinity and conductivity at constant temperature, this is done by the conductivity probe in the TCA. Once this was accomplished, the working range determined under these laboratory conditions was from about $10 \mu\text{g L}^{-1}$ to $40 \mu\text{g L}^{-1}$, and the detected concentration had a precision of $\pm 3 \mu\text{g L}^{-1}$ at the $30 \mu\text{g L}^{-1}$ Cu level (Figure 4). Under both laboratory and industrial conditions the salinity (i.e., conductivity) and pH probes will be calibrated manually by removing the probes from their respective chambers, and immersing them in appropriate buffers or standard solutions.

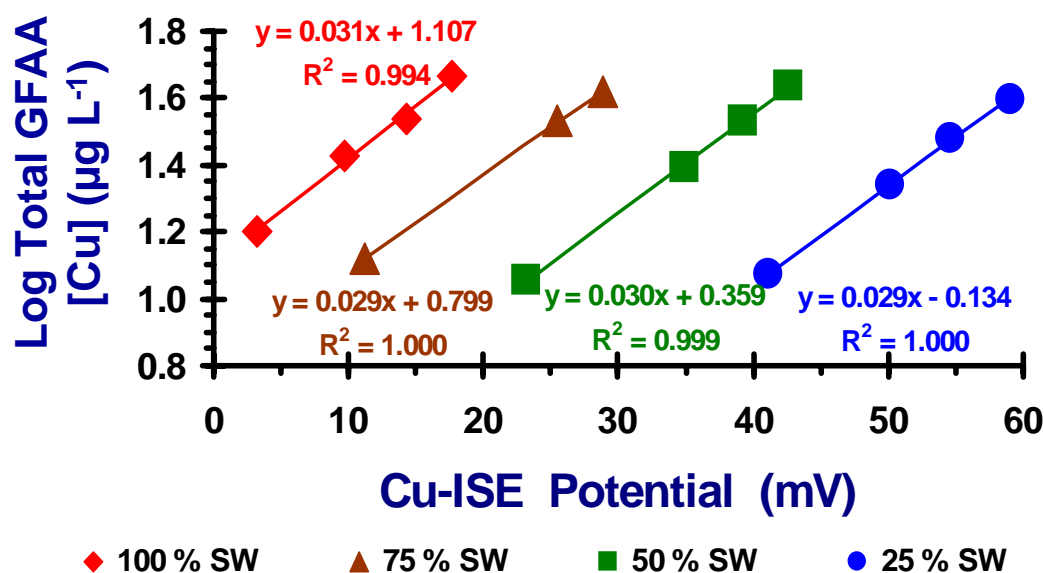


Figure 3 Calibration curves of the potential (mV) measured with the Jalpaite Cu-ISE in a prototype TCA and the total copper concentration measured by GFAA.

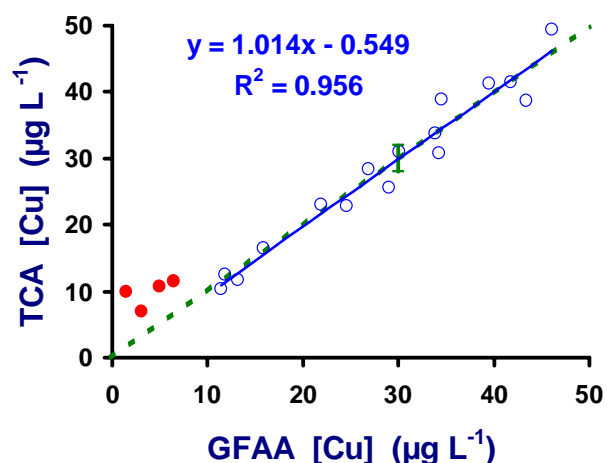


Figure 4 Comparison of copper concentrations measured with the TCA with those measured by GFAA in a suite of mixtures of seawater and freshwater under laboratory conditions. The filled red circles are data not used for the regression. The green dashed line indicated the optimal response of 1:1.

2.3 Factors Affecting Cost and Performance

Cost and performance of the TCA will be affected by several factors, including: (i) training requirements for operation of the instrument, (ii) acquisition, handling and preparation of reagents needed, (iv) improvements/modifications to facilities to fulfill the required environmental conditions for the TCA, and (iii) costs of operation and maintenance of the TCA.

2.4 Advantages and Limitations of the Technology

The main advantage of the TCA is the capacity to measure total recoverable copper *in situ* in real-time. This is a great advantage over conventional procedures, which require sampling, shipping to commercial laboratories and analysis, which is an expensive process with a turnaround period of at least two weeks.

A limitation of the TCA is the need for a reference electrode. As the potential is measured between the Cu-ISE and a reference electrode, the actual measurement is not absolute, but relative. That is, the measured potential could vary when different reference electrodes are used. Therefore, it is of great importance to keep the characteristics of the reference electrode intact for the longest time interval possible. In the case of the TCA this is done by using an industrial reference electrode with high-volume of internal reference solution.

The TCA requires about a week for equilibration with the effluent also requiring a separate measurement of the copper concentration in the effluent by other means in order to calibrate the instrument. In the three sites for the demonstration, one-week was needed for the TCA to reach baseline response; this lapse of time is needed to purge the TCA of any source of metal in order to measure the concentrations in the discharge. The calibration is accomplished with a computer controlled calibration pump and a standard of known copper concentration. Once the signal in the TCA is stable, the standard will be pumped at three different flow rates, each one adding a specific amount of copper to the sample. This information will be used in conjunction with the measured copper concentration to create a standard additions calibration of the copper concentration in the sample.

As the TCA continuously pumps effluent throughout its system, a volume of effluent is always required for its operation. The sites tested presented no problem with respect to this requirement; however, there could be the case of sporadic effluents that cannot fulfill this requirement. This could be overcome with the use of a recirculation system, but this was not addressed in this demonstration.

The TCA is affected by extreme changes in temperature. Initial laboratory studies indicated that the TCA is only affected when the ambient temperature of the location of the TCA was below 23 °C. However, the demonstration at the SBWWTP showed that extreme ranges in temperature, even above 23 °C, could affect the response of the instrument. Therefore, another limitation of this technology is the requirement of infrastructure with fairly constant temperature (i.e., a room or site not affected by large changes in temperature).

3. Demonstration Design

3.1 Performance Objectives

The performance objectives for this demonstration are shown in Table 2. These objectives are based on performance and maintenance/operation of the TCA. They are designed to provide enough sensitivity and dynamic range for the use of the TCA in industrial settings, with regulatory requirements for copper in the order of few $\mu\text{g L}^{-1}$.

Table 2 Performance objectives for the demonstration of the TCA in industrial situations at PSNS, PHNS, and SBWWTP.

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance Objective Met?
Quantitative	1. Evaluate limit of detection	$\leq 10 \mu\text{g L}^{-1} \text{ Cu}$	YES
	2. Evaluate working range of TCA	10 to 50 $\mu\text{g L}^{-1} \text{ Cu}$	YES
	3. Evaluate precision of Cu measurement	$\pm 10\%$ at 30 $\mu\text{g L}^{-1}$ level.	YES
	4. Evaluate reliability of measurements	$\pm 15\%$ within working range	NO
	5. Cost of operation	$< \$3\text{K per year}$	NO
Qualitative	1. Evaluate factors affecting TCA performance	Quantitative criteria at different salinities	YES
	2. Evaluate reliability of TCA	Maintenance at monthly interval	NO

3.2 Selecting Test Sites/Facilities

The main criterion used for the selection of demonstration sites was the need for continuous monitoring of total recoverable copper concentrations in its discharges. Therefore, the selected sites are required by regulatory agencies for the monitoring and controlling of copper in their discharges. This is the case with the dry docks at PSNS; where as mentioned above a NPDES permit allows a daily maximum limit of total recoverable copper of 33 $\mu\text{g L}^{-1}$, with a monthly average of 19 $\mu\text{g L}^{-1}$. In the case of the dry docks at PHNS a recently established interim NPDES permit allows a daily maximum limit of total recoverable copper of 23 $\mu\text{g L}^{-1}$.

The effluent at SBWWTP was selected in compliance with the Environmental Security Technology Certification Program (ESTCP) requirement to include a DoD non-Navy site. Several locations were considered for demonstration, and SBWWTP fulfilled the two main criteria for the demonstration. In this case the criteria were public concern of copper loading, and continuous discharge of freshwater effluent. Operators of the SBWWTP have

interest in the fate of copper through the treatment process, and are interested in finding out the sources of copper through this process.

The complexity in the industrial setting at the dry docks was expected to provide a range and variation in the copper concentrations of their discharges. This is supported by the copper concentrations measured at the effluents from PSNS (Figure 6) and PHNS (Figure 7) as part of their NPDES permits. The effluent at SBWWTP presented the opportunity of testing the TCA in a freshwater effluent.

The dry docks have good infrastructure for the deployment of the TCA. In both cases the TCA was deployed in the Pump Well, which is a six story deep subterranean structure at the side of the dry dock, with pumping and controls for water and electrical systems. This structure is isolated from the outdoor environment, and remains at fairly constant conditions of temperature and humidity therefore the temperate conditions in the Pump Well allowed for more stable response by the instrument. They also have access to a continuous source of effluent, in the case of PSNS a mixture of water from the adjacent Sinclair Inlet and the effluent, and in the case of PHNS effluent in the sump at the bottom of the dry dock.

In contrast to the dry docks, where the TCA was under constant temperature and humidity, the location chosen for the placement of the TCA (i.e., a plastic-made hut located outdoors) at SBWWTP had an extreme range in temperature throughout the day. This extreme range of temperatures affected the response of the instrument, and guided for the inclusion of the temperature-effect limitation for the use of the TCA.

3.3 Test Site/Facility History/Characteristics

Three DoD sites were selected for the demonstration of the TCA, the dry docks at PSNS and PHNS, and the wastewater treatment plant at Schofield Barracks. PSNS is located adjacent to the City of Bremerton in western Washington, was established in 1891 and is the Pacific Northwest's largest Naval Shore Facility and one of Washington's largest industrial installations. The shipyard and the adjacent Naval Base Bremerton encompass 353 acres of land, 360 buildings, six dry docks, and nine piers with more than 2 miles of deep-water space. Dry dock 6, used for this demonstration, is the largest dry dock owned by the Navy. The current mission of PSNS is maintenance for ships Navy-wide, including overhaul, repair, and recycling, and engineering design work. Additionally, PSNS serves as a homeport for several ships.

As its name denotes, PHNS is located in Pearl Harbor on the island of Oahu, Hawaii. The shipyard was established in 1908 and is the largest repair facility in the Pacific. In conjunction with the Intermediate Maintenance Facility (IMF), they form the largest industrial complex in Hawaii. The command encompasses 300 acres of land, 158 buildings, 4 dry docks, and 34 piers. There are six outfalls for the four dry docks at PHNS, and dry dock 2 was used for the demonstration. The mission of PHNS is to provide maintenance to submarines and surface craft, including submarine maintenance, modernization, inactivation, surface ship complex overhaul, voyage repairs, and Pacific Fleet support.

Schofield Barracks is the largest Army's installation outside the continental United States. It was established in 1908 to provide a base for the Army's mobile defense of the island of Oahu. It is located in the Schofield Plateau between the Waianae and Koolau Ranges, near the town of

Wahiawa in central Oahu. With an area of 17,725 acres, it is surrounded by rain forest, and it is used for housing, training and industrial operations. Schofield Barracks houses the 25th Infantry Division (Light) unit, the Army Garrison, Hawaii; 703rd Military Intelligence Brigade; 45th Corps Support Group (Forward); and the Hawaii National Guard. The base had a large population of about 12,005 active-duty personnel with 11,380 family members, along with 3,000 Guard, 1,273 Reserve and 2,673 civilians. Housing offers 667 officer-family units, 4,687 enlisted-family units, 36 unaccompanied officer units and 26 unaccompanied enlisted units. Temporary lodging is also available, offering 192 guest house units. Industrial operations involved maintenance, repair, painting, and degreasing.

3.4 Present Operations

The activities at PSNS generate wastewater such as bilge water, storm water runoff, and industrial wastewater subject to federal, state, and local regulatory requirements. The operation and handling of discharges in dry docks is very complex (Figure 5). In the case of PSNS, as stated above, a NPDES permit regulates the discharge of copper to $33 \mu\text{g L}^{-1}$ from dry dock operations; however, in the past this limit was sometimes exceeded, as indicated by Figure 6, which shows the total recoverable copper concentration in a discharge from PSNS dry docks.

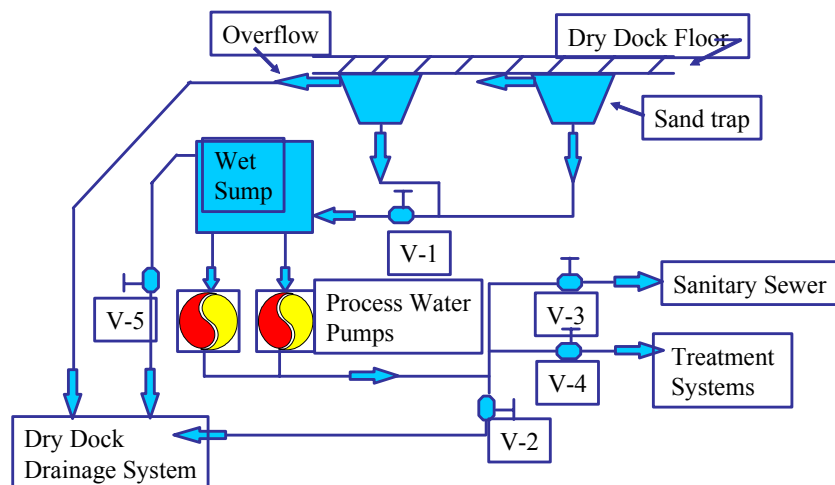


Figure 5 Diagram of drainage systems in a dry dock at PSNS.

In order to avoid these exceedances the current approach is to collect discrete samples automatically, which provides an incomplete picture of the drainage system in dry dock 6. Furthermore, water discharges at PSNS are massive and complex, with up to 600,000 gallons day^{-1} in one discharge, made up of storm water, process water, seawater leakage, freeze protection water, and ship discharges. Therefore, without a real-time continuous monitoring, the only option is treatment of all the discharge, which, at a cost of $\$0.11 \text{ gallon}^{-1}$, can add up to $\$66,000 \text{ day}^{-1}$.

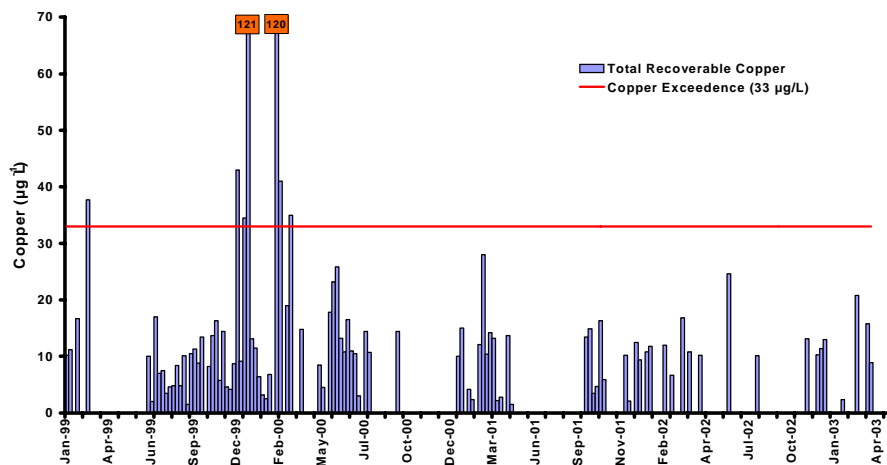


Figure 6 Total recoverable copper concentrations ($\mu\text{g L}^{-1}$) measured in a discharge from dry dock 6 at PSNS.

The activities at PHNS generate wastewater such as bilge water, storm water runoff, and industrial wastewater subject to federal, state, and local regulatory requirements. As stated above, an interim NPDES permit regulates the discharge of copper to $23 \mu\text{g L}^{-1}$ from dry dock operations; however, this limit is sometimes exceeded, as indicated by Figure 7, which shows the total recoverable copper concentration measured in discrete samples from discharge B from dry dock 2 at PHNS from May 1996 to May 2003.

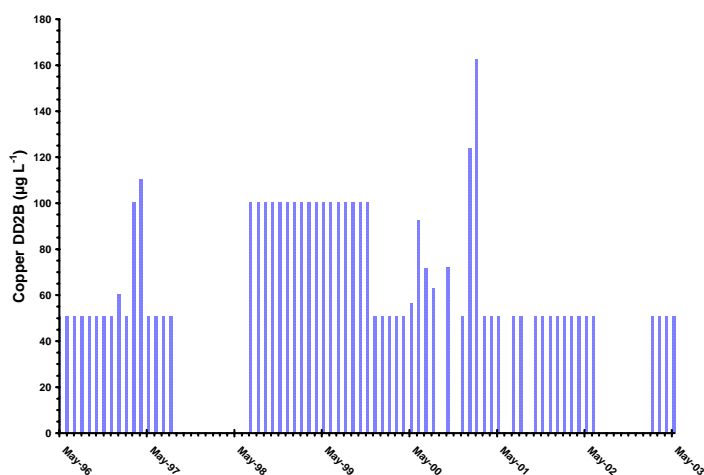


Figure 7 Total recoverable copper concentrations ($\mu\text{g L}^{-1}$) measured in discrete samples from discharge B of dry dock 2 at PHNS.

As Figure 7 indicates, the proposed discharge limit at PHNS was exceeded in the past. However, this information is misleading as they only represent the reporting requirements at those dates, and they are given as either <100 or $<50 \mu\text{g L}^{-1}$. The results from both the demonstration at the industrial sites and from laboratory experiments indicate that the TCA is able to provide concentrations well below these limits of detection, *in situ* and at near real time.

The U.S. Army Directorate of Public Works (DPW), SBWWTP, provides secondary treatment for Helemano Military Reservation, Wheeler Army Airfield, Schofield Barracks, and Schofield Barracks East Range. The SBWWTP is a fully functional, stand-alone wastewater treatment facility that operates 24 hours per day, 365 days per year, with a typical influent flow of 2.4×10^6 gal day⁻¹. A schematic diagram of the treatment operations at SBWWTP is provided in Figure 8. The TCA was demonstrated in the effluent after the final sand filtration, but prior to the chlorination step. This is done because the oxidative characteristics of bleach are known to affect the response of the Cu-ISE.

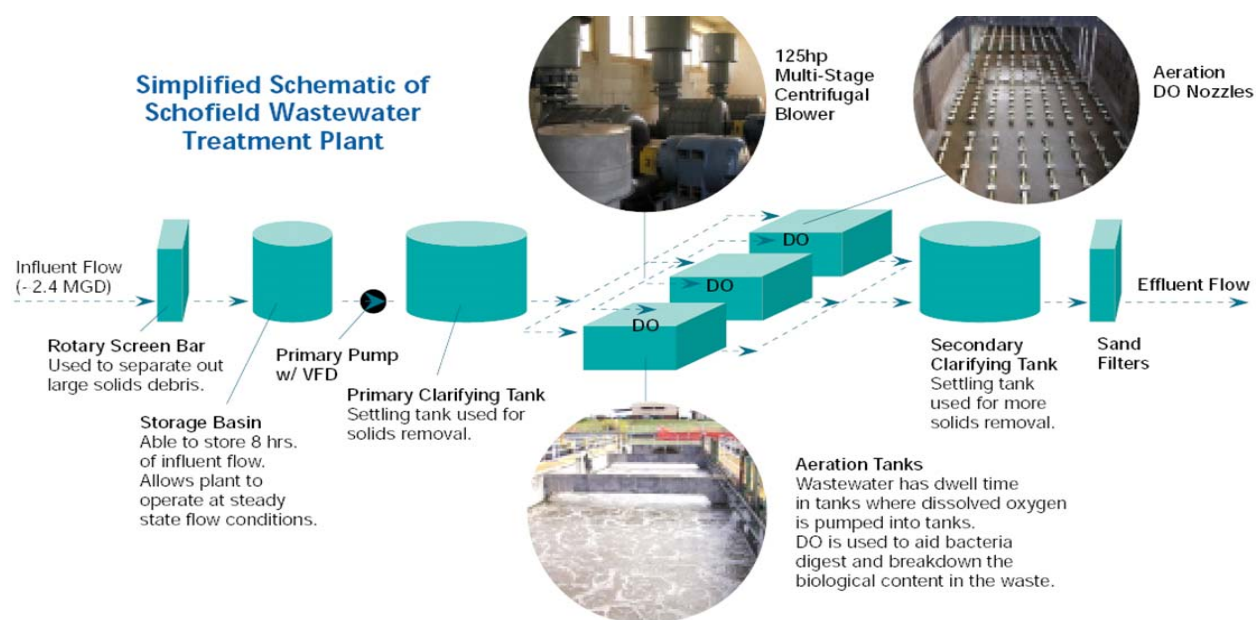


Figure 8 Diagram of the treatment process at SBWWTP. The TCA will be demonstrated in the effluent flow after the final sand filtration and prior to chlorination.

The treated effluent has relatively stable physical and chemical characteristics. Figure 9 shows some of the characteristics of the effluent, and it indicates that most of these characteristics remain relatively stable through time. Total copper concentration is not included in Figure 9 as there is not regulatory requirement for its measurement. Being a freshwater effluent, in comparison to the saltwater effluents where the TCA was demonstrated in the dry docks, the effluent at the SBWWTP did provide a different set of stable physical and chemical characteristics for the demonstration of the TCA.

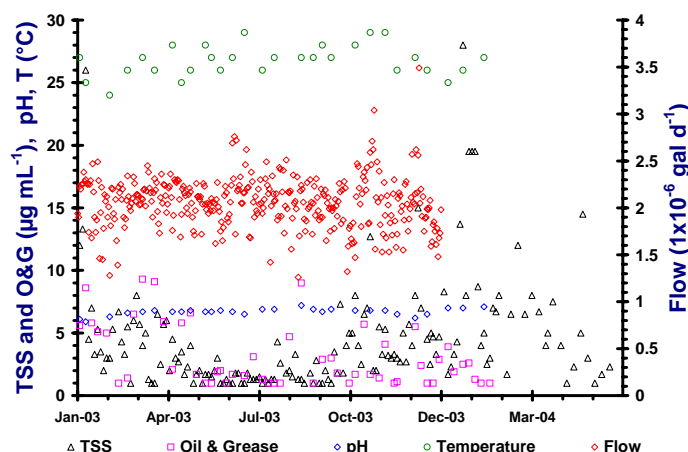


Figure 9 Physical and chemical characteristics of the effluent at the SBWWTP: TSS; $\mu\text{g mL}^{-1}$, O&G ($\mu\text{g mL}^{-1}$), pH, temperature ($^{\circ}\text{C}$), and flow ($1 \times 10^6 \text{ gal day}^{-1}$).

3.5 Pre-Demonstration Testing and Analysis

There was no pre-demonstration testing done specifically for the use of the TCA at the demonstration sites. In the dry docks there is a requirement by regulatory enforcement on the collection of discrete samples for the evaluation of copper concentration in the effluent. The information from such effort is presented in Figures 6 and 7, and could be used as baseline for the demonstration of the TCA. For the case of SBWWTP, there is no regulatory requirement for the evaluation of copper concentrations in its effluent. Instead of using the historical data for the dry docks, and due to the lack of information at SBWWTP, it was opted for the collection of discrete samples in duplicate at the time of the deployment at each site, and to have these samples analyzed at a commercial laboratory and at government facilities. These discrete samples provide a real-time baseline for comparison with TCA measurements in all sites. As these samples were considered part of the demonstration, the data is presented with the information from the actual demonstrations.

3.5.1 Laboratory Characterization

Concurrent with the demonstrations, there was extensive testing of the TCA under laboratory conditions at SSC-SD. The testing included long-term continuous measurement with water from San Diego Bay and with deionized water (DI). The long-term continuous measurement of total recoverable copper in seawater from San Diego Bay was done in order to create a baseline response of the instrument at levels presumed below its limit of detection. Total recoverable copper concentrations in this area of San Diego Bay are in the order of less than $1 \mu\text{g L}^{-1}$. This long-term testing also provided information on the effects of salinity and temperature, the reliability of the TCA, and the time interval between maintenance efforts. The long-term measurement with deionized water allowed for the control of parameters required for the evaluation of dynamic range, sensitivity, and of interference by other heavy metals and humic acids. Further concurrent testing was done to measure the flow rates of the different pumps that are part of the TCA.

3.5.1.1 Long-term Laboratory Characterization with San Diego Seawater

The long-term laboratory characterization study with seawater from San Diego Bay was done between November 2002 and June 2003 on a small floating instrument hut located near the stormwater outflow into San Diego Bay. Average salinity for this area of San Diego Bay has been reported to be 33.7 (Chadwick *et al.*, 2004). Initially the TCA was set to measure copper concentrations in the seawater from the bay; but, these measurements provided very complex data as a result of simultaneous variations of several parameters (Figure 10). In general, the response of the Cu-ISE seemed to follow very closely changes in room temperature and tidal variation. Temperature variations were due to daily fluctuations between day and night in the instrument hut, and tidal effects are assumed due to copper sources from neighbor semi-enclosed marinas located upstream during ebb tide. Therefore, it was opted to work from large batches of seawater and mixtures of seawater and deionized water to study the response of the TCA to different salinities (i.e., conductivity; Figure 11). The results from this characterization corroborated the previously observed effect of conductivity (i.e., salinity) on the response of the Cu-ISE (Figure 3), with a change in the baseline potential at different conductivities (Figure 11). As Figure 12 shows, the Cu-ISE potential (mV) measured at very low copper concentrations changes linearly as a function of the conductivity (i.e., salinity).

In contrast the response of the TCA with temperature is complex. A large batch of artificial seawater (ASW), made of 3.2% NaCl in DI (salinity 32) at pH 2 and no copper, and dilutions of this were set in the floating instrument hut, in order to keep most parameters constant, but the temperature. The results indicate a complex pattern of response as a function of temperature at constant salinity (Figure 13), with lower than 50% salinity seawater showing an increase in the Cu-ISE response with decrease in temperature, at temperatures below 20°C. However, these results also indicate that there is no significant effect at temperatures above 20°C. And, since the ultrasonic digestion generates enough heat to keep the TCA at temperatures above this threshold, effects due to temperature were considered minimized in the instrument.

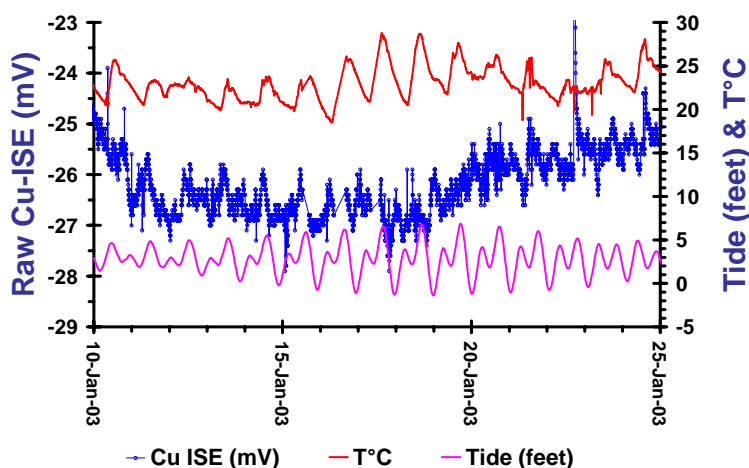


Figure 10 Response of the TCA to seawater from San Diego Bay. The response is represented as the potential (mV) measured by the Cu-ISE. The complex pattern seems to follow both temperature and tidal effects.

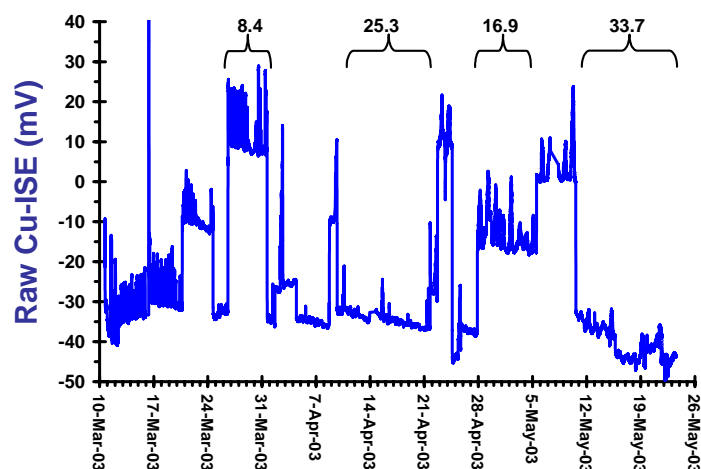


Figure 11 Effect of salinity (i.e., conductivity) on the response of the Cu-ISE. The TCA was fed with mixtures of seawater from San Diego Bay and deionized water in order to model the salinity of the water. Salinities are given at the top of the figure.

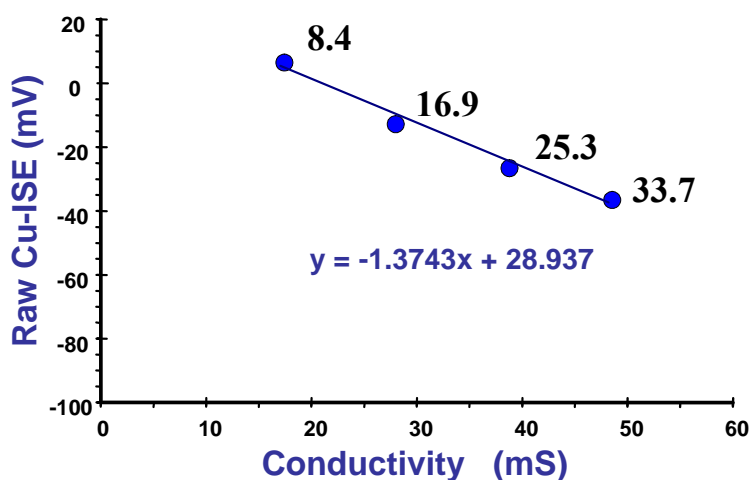


Figure 12 Baseline Cu-ISE potential (mV) observed at background concentrations (i.e., less than one $\mu\text{g L}^{-1}$) throughout a long-term laboratory characterization experiment with the TCA in waters of San Diego Bay at different salinities. Salinities are given for each of the observed potentials.

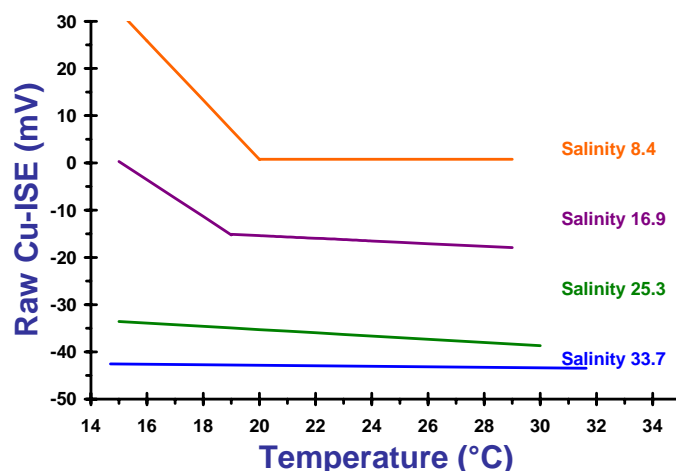


Figure 13 Response of the Cu-ISE to changes in temperature at constant salinity and copper concentration. These are regressions of the data for the corresponding range of temperature at specific salinity.

3.5.1.2 Long-term Laboratory Characterization with DI

The dynamic range of the TCA and the effects of possible metal and organic interferences were evaluated with DI under a laboratory setting. The TCA was connected to the DI system in the laboratory building at SSC-SD from May 2004 to June 2005. Once the TCA response was stabilized, tests for precision, dynamic range and effect by possible interferences were conducted. This was done by injection of copper standards or the interferences. Figure 14 shows part of the deployment in DI, and includes data for multiple single copper concentration injections and automatic calibrations of the TCA.

The total recoverable copper concentration is calculated in the TCA using a calibration curve, or direct method. The baseline of the calibration is established once the TCA is equilibrated with the sample, and then the calibration is done by adding four pre-set volumes of a high copper concentration standard. The copper standard is made by dilution of a GFAA or ICP-MS grade copper standard in DI that contains an amount of sodium chloride similar to that expected in the sample. The potentials (mV) at the different copper concentrations added are used to determine the slope (b) and the intercept (a) of the calibration curve. And the total recoverable copper is determined as follows:

$$[Cu](\mu g L^{-1}) = 10^{[(mV \times b) + a]}$$

The results of the series of automatic calibrations performed from 4 to 10 May indicate a precision better than $\pm 3 \mu g L^{-1}$ at the $30 \mu g L^{-1}$ level. The total recoverable copper concentrations for the 15 automatic calibration curves were calculated using the average slope and intercept of them and are shown in Table 3. The calculated concentrations indicate a precision better than $\pm 10\%$ for concentrations of 20, 30 and $40 \mu g L^{-1}$, and a precision of $\pm 12.8\%$ for $10 \mu g L^{-1}$ total recoverable copper. The precision here is given as one standard deviation of the estimated concentration. This fulfills the performance objective criteria (Table 2) of $\pm 10\%$ at a $30 \mu g L^{-1}$ concentration level.

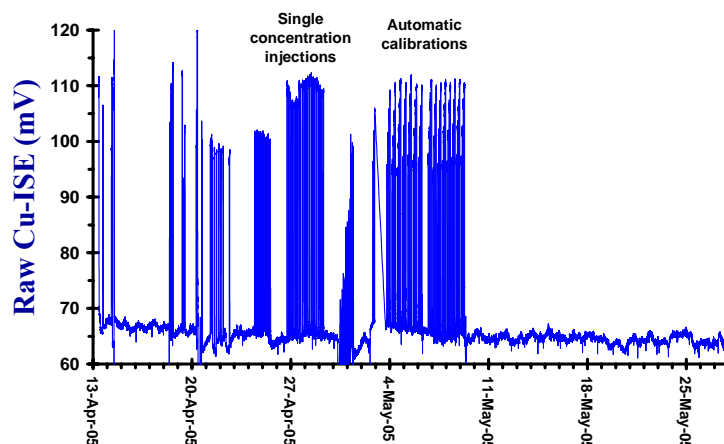


Figure 14 Response of the TCA in DI. The response was evaluated as the potential (mV) measured by the Cu-ISE. The data includes multiple injections of single copper concentrations, and multiple automatic calibrations used for the characterization of the TCA.

Table 3 Average and one standard deviation for the concentrations estimated for 15 automatic calibrations in deionized water.

[Cu] added ($\mu\text{g L}^{-1}$)	Cu-ISE Potential (E) (mV)		Estimated Total Recoverable copper ($\mu\text{g L}^{-1}$)		Precision ($\pm\%$)
	Average	Standard deviation	Average	Standard deviation	
10	95.9	1.37	10.6	1.3	12.8
20	101.8	0.78	18.5	1.3	6.5
30	106.7	0.73	29.8	2.1	6.8
40	110.2	0.85	41.7	3.3	8.3

The single concentration injections of $40 \mu\text{g L}^{-1}$ copper performed from 27 to 29 May 2005 have a precision of $\pm 16\%$. The average and one standard deviation for the 23 single concentration injections were $37.5 \pm 6.53 \mu\text{g L}^{-1}$, which is 16.3% of the $40 \mu\text{g L}^{-1}$ copper concentration injected. This indicates that the response of the TCA could be affected by other factors. In this case there is the suspicion that the calibration pump in the instrument was responsible for this result.

The dynamic range of response of the TCA was evaluated as the response (mV) of the Cu-ISE to additions in DI with no NaCl added, and with 3.2% NaCl. The latter was done as an approximation to seawater. The dynamic range in DI is from $0.5 \mu\text{g L}^{-1}$ (-8.1 Log Cu) to $400 \mu\text{g L}^{-1}$ (-5.2 Log Cu ; Figure 15), while that in 3.2% NaCl is $2 \mu\text{g L}^{-1}$ (-7.5 Log Cu) to $400 \mu\text{g L}^{-1}$ (Figure 16). It should be mentioned that the response was still linear at $400 \mu\text{g L}^{-1}$, and that no effort was undertaken to extend the study beyond this upper limit.

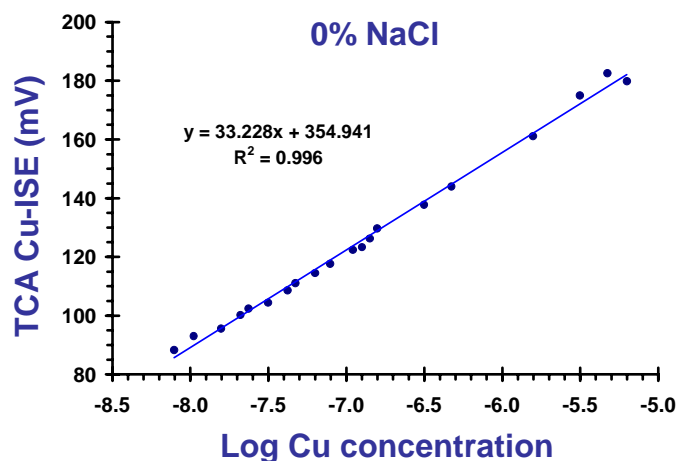


Figure 15 Dynamic range of the TCA in DI. The TCA had a linear response from a log of copper concentration of -8.1 ($0.5 \mu\text{g L}^{-1}$) to -5.2 ($400 \mu\text{g L}^{-1}$).

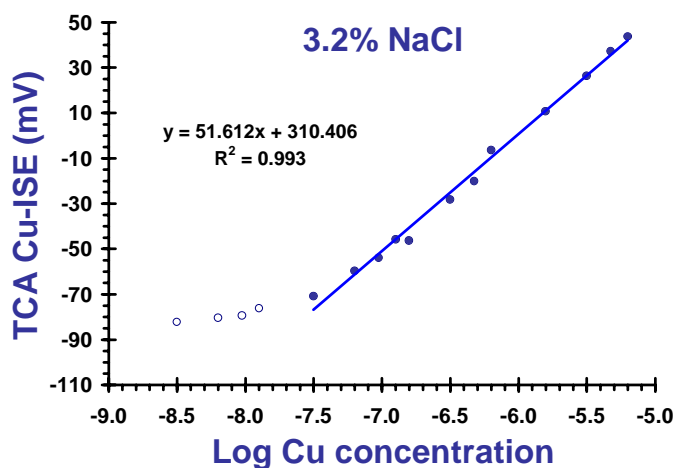


Figure 16 Dynamic range of the TCA in artificial seawater (i.e., DI with 3.2% NaCl, salinity 32). The TCA had a linear response from a log of copper concentration of -7.5 ($2 \mu\text{g L}^{-1}$) to -5.2 ($400 \mu\text{g L}^{-1}$).

A result from the demonstration in PSNS was the replacement of $\frac{1}{4}$ " inside diameter (ID) to $\frac{1}{8}$ " ID Teflon[®] tubing, in order to decrease the lag in the response of the TCA. This lag is mainly due to the travel time of the effluent throughout the TCA, and it was of about 11 minutes with $\frac{1}{4}$ " ID Teflon[®] tubing. Figure 17 shows the response of the Cu-ISE to the injection of $30 \mu\text{g L}^{-1}$ copper for 45 minutes when the TCA was equipped with $\frac{1}{8}$ " ID Teflon[®] tubing, and the TCA is connected to a DI water source. In spite of the fact that the Cu-ISE reacted within a couple of minutes with an approximately $25 \mu\text{g L}^{-1}$ response, it took the electrode about 25 minutes to reach the $30 \mu\text{g L}^{-1}$ response. In contrast, once the injection of $30 \mu\text{g L}^{-1}$ was stopped, the lag in the response was decreased to about 5 minutes as compared to 11 minutes for the $\frac{1}{4}$ " ID Teflon[®] tubing (Figure 17).

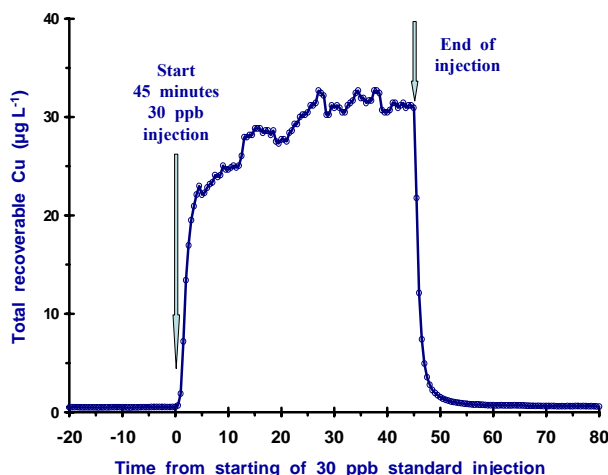


Figure 17 Automatic spiking of 30 $\mu\text{g L}^{-1}$ copper for 45 minutes, when the TCA is equipped with $\frac{1}{8}$ " ID Teflon[®] tubing. The lapse interval to reach this concentration was 25 minutes, with 5 minutes needed to reach baseline concentration at the end of the spiking. Measured on 25 March 2005 during the characterization with deionized water.

3.5.1.3 Interference by Metals and Humic Acid

The effects of the metals zinc (Zn), manganese (Mn), cadmium (Cd), iron (Fe) and chromium (Cr) as interferences on the TCA response were investigated by injection of high concentrations into an artificial seawater sample matrix containing copper. Variations (increase or decrease) in the Cu-ISE potential (mV) was used as an indication of the interference by the added metal or humic acid and further investigations were performed to characterize the nature of the effect. The metals were injected from 1000 $\mu\text{g L}^{-1}$ acidified solutions, commercially available as GFAA or ICP standards, at specific flow rates set to reach the desired spiking concentration in the sample stream. The artificial seawater matrix was DI with 3.2% sodium chloride, containing 25 $\mu\text{g L}^{-1}$ copper, with the pH adjusted to pH 2 with HNO_3 .

No effect on the response of the Cu-ISE was observed for the additions of Mn, Zn and Cd (Figure 18). The metal concentrations in the sample stream after injections were 12.5, 25, 37.5 and 50 $\mu\text{g mL}^{-1}$ (micrograms per milliliter or parts per-million, ppm) for Mn and Zn, and 7.5, 15, 22.5 and 30 $\mu\text{g mL}^{-1}$ for Cd. And, in spite of having concentrations three orders of magnitude above that for copper (25 $\mu\text{g L}^{-1}$) the potential of the Cu-ISE remained essentially unchanged.

In contrast to Mn, Zn and Cd, both Fe and Cr showed effects on the response of the Cu-ISE. The Fe and Cr injections were stopped after the second and first injections, respectively, when it was observed that the Cu-ISE responded significantly to these two metals (Figures 19 and 20). In the case of Fe, there was an increase in the Cu-ISE potential, indicating that the Cu-ISE responds to increases of this element (Figure 19). Addition of Cr(VI) poisoned the electrode, as shown by the increase and then a decrease of the signal (Figure 20), indicating that the TCA can not work in presence of this metal, and no further studies were done with Cr.

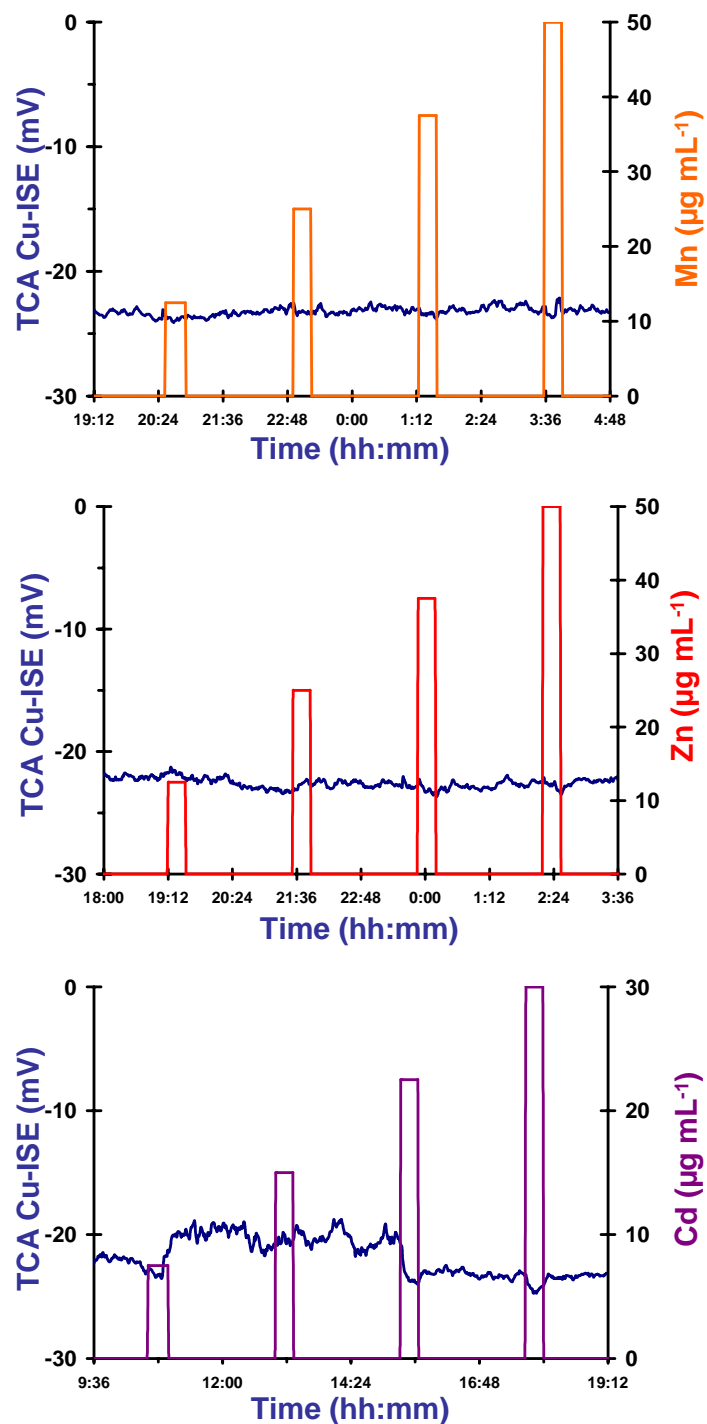


Figure 18 No effect on the response of the TCA's Cu-ISE was observed to additions of Mn (top plot), Zn (middle plot) and Cd (bottom plot). The solution matrix is $25 \mu\text{g L}^{-1}$ copper in artificial seawater (DI with 3.5% NaCl, salinity 35) at pH 2. The injected quantities of Mn, Zn, and Cd were 12.5, 25.0, 37.5, and $50.0 \mu\text{g mL}^{-1}$.

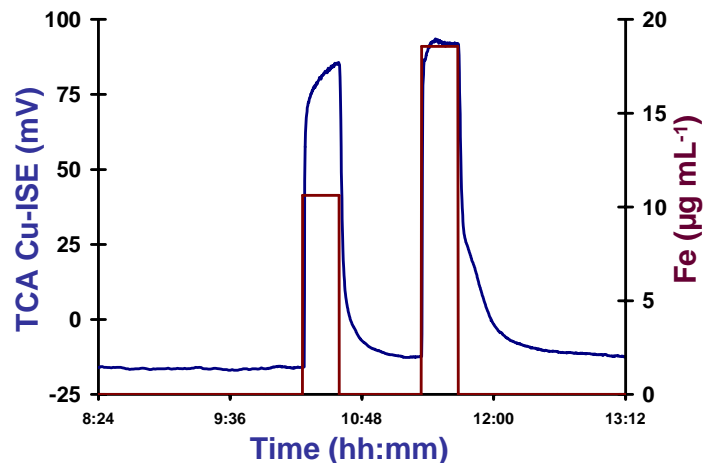


Figure 19 Effect of 10 and 17.5 $\mu\text{g mL}^{-1}$ Fe addition on the Cu-ISE response, in DI with 3.5% NaCl (salinity 35), with 25 $\mu\text{g L}^{-1}$ copper and pH 2.

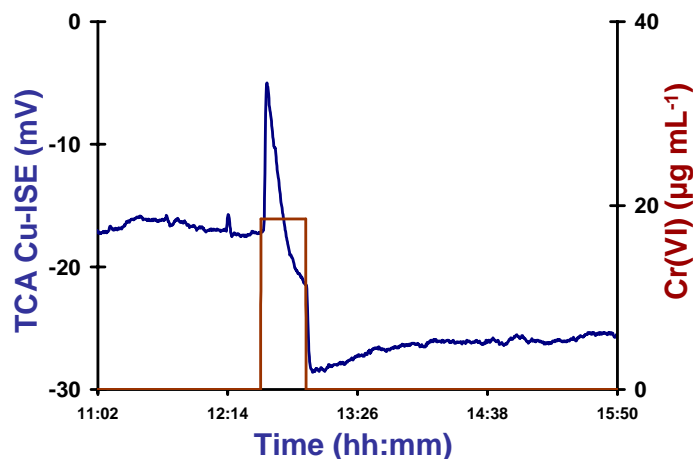


Figure 20 Effect of 20 $\mu\text{g mL}^{-1}$ Cr (VI) on the response of the Cu-ISE in DI with 3.5% NaCl (salinity 35), with 25 $\mu\text{g L}^{-1}$ copper and pH 2.

Further study of Fe as an interferent to the Cu-ISE was done by measuring copper response in a sample matrix containing Fe. Cu-ISE response was compared to the response to copper in a sample stream with no Fe. Solutions of 100, 250 and 500 $\mu\text{g L}^{-1}$ Fe in DI with 3.2% NaCl (salinity 32) at pH 2 were prepared in bulk then fed to the TCA. At regular intervals a solution of 1000 $\mu\text{g L}^{-1}$ copper was injected into the sample stream to arrive at injected copper concentrations of 10, 20, 30 and 40 $\mu\text{g L}^{-1}$ copper. The acid and sodium chloride concentrations of the injected copper solution had been adjusted to match those of the matrix, therefore, diminishing possible matrix effects. The results were processed as normally done for a calibration of the TCA. A linear regression was performed on the variables log Cu concentration and observed Cu-ISE potential. Suppression is calculated by comparison of the slopes (Table 4).

A signal suppression of 31, 67 and 81% was measured for 100, 250 and 500 $\mu\text{g L}^{-1}$ Fe matrices, respectively.

Table 4 Decrease in the Cu-ISE potential observed for calibration curves made in artificial seawater (3.2% NaCl in DI at pH 2, salinity 32) with different Fe concentrations.

Fe $\mu\text{g L}^{-1}$	Cu-ISE Baseline (mV)	Cu-ISE at [Cu] 25 $\mu\text{g L}^{-1}$ (mV)	Slope	Intercept	Suppression (%)
0	-83.2	60.4	60.7	366.2	
100	-48.0	41.7	48.6	304.7	31
250	-29.6	19.8	27.0	163.3	67
500	-15.9	11.7	16.7	102.6	81

The response of the TCA to the presence of organic material was studied in bulk samples with different concentrations of humic acids (0, 1, 5, and 10 $\mu\text{g mL}^{-1}$) in DI at pH 2. The effect was measured as the change in the response to copper calibrations (10, 20, 30, and 40 $\mu\text{g L}^{-1}$ Cu) in each one of the humic acid samples. A Cu calibration was done at each humic acid concentration, and the change in the slope of the calibration is used to estimate the change in sensitivity. The presence of humic acids resulted in a decrease in the sensitivity of the TCA of 16% at 5 $\mu\text{g mL}^{-1}$ humic acid (Figure 21).

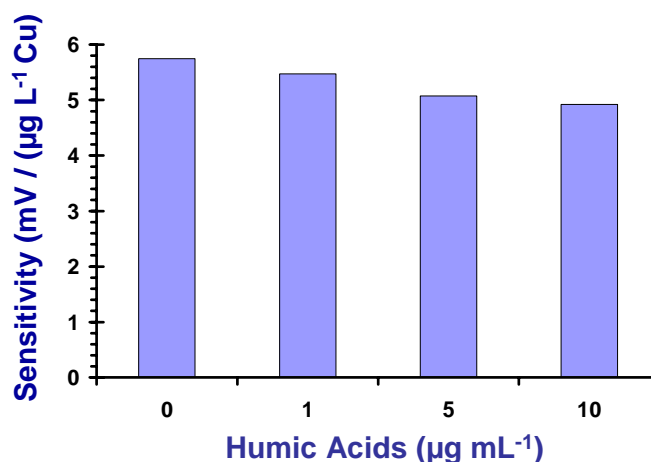


Figure 21 Effect of humic acids (i.e., organic matter) on the sensitivity of the TCA. The matrix is DI at pH 2. The sensitivity is measured as a change in slope for Cu calibrations (10, 20, 30, and 40 $\mu\text{g L}^{-1}$ Cu) at each humic acid concentration. A 16% decrease in the response was observed at 5 $\mu\text{g mL}^{-1}$ humic acids.

3.6 Testing and Evaluation Plan

3.6.1 Demonstration Set-Up and Start-Up

The TCA was shipped to each of the three demonstration sites in turn. Once the instrument arrived, it was unpacked, assembled and calibrated by personnel from SSC-SD. The TCA was set at the location designated by personnel at each site, and connected to the appropriate sampling port provided at each site. Operating conditions required by the TCA include a 110 AC / 15 Amps power source, an area of about 6 by 8 feet, a sampling port connection to the effluent, and a discharge port. The discharge port of the TCA was directed to the municipal sewer system in the cases of PSNS and PHNS, and to the discharge stream before the chlorination step at SBWWTP.

In order to measure performance of the TCA between maintenance cycles, a 30-day maintenance cycle was observed at all sites. The goal was to have the instrument working for at least a month interval between maintenance events. Due to the need for calibration and collection of discrete samples for analysis by Battelle and SSC-SD, personnel from SSC-SD were at the demonstration site in the second and fourth weeks of deployment. As the TCA requires a supply of weak nitric acid, the required contact information, hazardous material labeling, material safety data sheets, and secondary containment was used or provided at each demonstration site.

3.6.2 Period of Operation

The dates for the demonstration at PSNS were from 7 July to 15 August, 2003. The TCA was shipped to PSNS on 26 June, 2003. Personnel from SSC-SD arrived at Bremerton on 5 July, and proceeded with installation and initial calibration of TCA from 7 July to 15 July, 2003. Personnel from SSC-SD monitored the response of the TCA throughout the demonstration. Nine duplicate discrete samples were collected from 21 to 24 July and from 12 to 14 August. At the end of the demonstration on 15 August, 2003, the TCA was taken apart, packed and shipped back to SSC-SD.

The demonstration at PHNS did occur between 24 February and 8 April, 2004. The TCA was shipped to PHNS in January 2004. Personnel from SSC-SD arrived at PHNS, and proceeded with installation and initial calibration of TCA. Nine duplicate discrete samples were collected from 3 to 5 March and from 5 to 7 April. At the end of the demonstration, the TCA was packed and shipped back to SSC-SD.

The dates for the demonstration at SBWWTP were from 12 July to 24 August, 2005. The TCA was shipped to Schofield Barracks in the first week of July 2005. Personnel from SSC-SD arrived at Schofield Barracks on 11 July, and proceeded with installation and initial calibration of TCA from 12 to 18 July, 2005. Personnel from SSC-SD monitored the response of the TCA throughout the demonstration, and collected discrete samples to be analyzed at Battelle and SSC-SD from 25 to 30 July and from 21 to 25 August. At the end of the demonstration, the TCA was taken apart, packed and shipped back to SSC-SD. Figure 22 is a Gantt chart of the dates for the three demonstrations.

As mentioned above, concurrent with the demonstrations there was a characterization of the TCA under laboratory conditions. This characterization was done with water from San Diego

Bay from November 2002 to June 2003, and with DI from May 2004 to June 2005. The characterization of the TCA under laboratory conditions is also depicted in Figure 22.

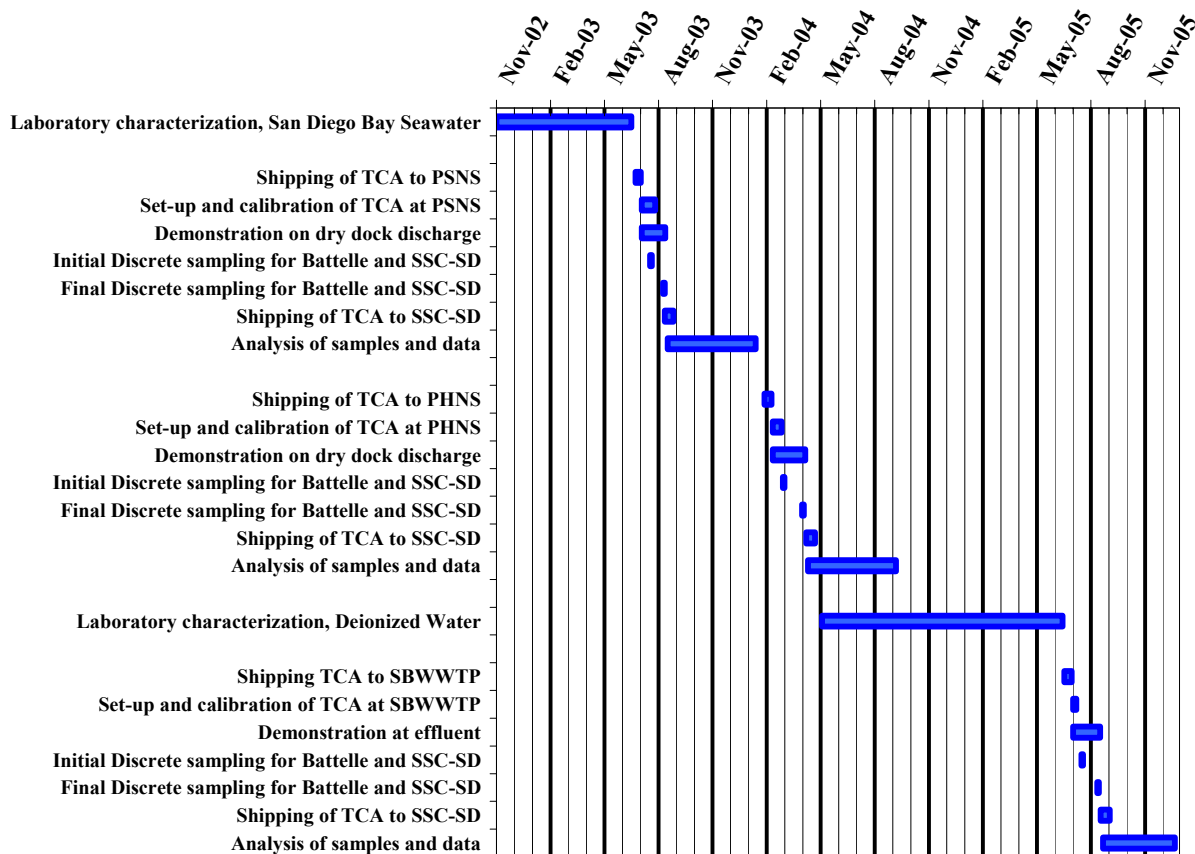


Figure 22 Gantt chart for dates of demonstrations of TCA at PSNS, PHNS and SBWWTP.

3.6.3 Amount/Treatment Rate of Material to be Treated

No materials were treated as a result of this demonstration.

3.6.4. Residuals Handling

The effluent from the TCA is neutral at pH 7, with an approximate temperature of 24°C and a flow rate of $\sim 14 \text{ mL min}^{-1}$. As the effluent from the TCA will only differ from that from the original effluent by 4.5×10^{-4} moles of sodium and 1×10^{-2} moles of nitrogen, it could be returned directly to the effluent stream. However, in the demonstrations at the dry docks the residual effluent from the TCA was directed into the municipal treatment system, and at SBWWTP it was directed to the effluent stream prior to chlorination.

3.6.5. Operating Parameters for the Technology

Operational requirements for the TCA include a source of power of 110 AC / 15 Amps, and appropriate connection to the effluent. The TCA is expected to work correctly at any ambient temperature between 10° to 40°C; however, the TCA requires a fairly constant ambient

temperature for optimal response. The TCA was operated continually for the time of the demonstration, and was able to be relocated as a unit as needed.

3.6.6 Experimental Design

The main objective of the demonstration was to evaluate the precision and accuracy of the TCA to measure total recoverable copper in the effluents from the dry docks at PSNS and PHNS, and from the treated effluent at SBWWTP, *in situ* and in near real-time. This was achieved by comparing the concentrations measured by the TCA in the effluents with those measured at Battelle and SSC-SD in grab samples from the same effluents. The analytical techniques used at these laboratories are included in Appendix A. The experimental design consisted of continuously running the TCA and recording the output at 30-second intervals, while systematically collecting discrete samples for measurement at Battelle and SSC-SD. The collection of samples was done on the second and on the final weeks of each deployment. Throughout the second week, grab samples (including all QA/QC duplicate, blank, and split samples) were collected every eight (8) hours, until a total of nine samples were collected. Nine samples were also collected 8 hours apart during the final week of the demonstration. These samples were used to examine any performance degradation at the end of the 30-day maintenance cycle. One set of the split samples was sent for copper concentration measurements each to the Battelle Marine Sciences Laboratory in Sequim, WA, and to the analytical laboratory at SSC-SD in San Diego, CA. The correspondence among the copper concentrations measured with the TCA and these two laboratories did provide the information needed to determine the precision and accuracy of the TCA.

A second objective of the project is to examine the cost of operating the TCA with a 30-day maintenance cycle. This objective was approached by recording all expenses including consumables and operator time during the scheduled one-month demonstration at the three sites.

3.6.7. Demobilization

The TCA is a semi-portable instrument, made up of three enclosures (Figure 1). The only hazardous material used with the TCA is nitric acid, and this should be disposed in accordance with the appropriate regulations. The instrument contains no hazardous materials and all wetted parts are Teflon, polyethylene, or stainless steel. Demobilization did consist of draining and rinsing the flow path of the TCA with clean water before detaching the three enclosures and packing them in specially made wooden crates for shipping or storage.

3.7 Selection of Analytical/Testing Methods

The analytical methods that were used in the demonstration of the TCA are the standard methods approved by U.S. EPA. These include: (1) Method 3020A, acid digestion of aqueous samples and extracts for total metals by analysis by GFAA (U.S. EPA, 1992); (2) Method 7211, measurement of Copper by atomic absorption furnace technique (U.S. EPA, 1992); and (3) Method 1640m, the measurement of metals by on-line chelation and ICP-MS (U.S. EPA, 1996). These methods are provided in Appendix A. Total recoverable copper concentrations in the effluent samples were measured at Battelle by ICP-MS and at SSC-SD by GFAA directly from the acidified samples of effluent.

3.8 Selection of Analytical/Testing Laboratory

The laboratories chosen for the analysis of the samples from the three sites are SSC-SD in San Diego, CA, and Battelle Marine Sciences Laboratory in Sequim, WA. These laboratories were chosen because they both have the extensive experience and the instrumentation required for the analysis of copper and other trace metals in aquatic matrices. The laboratory at SSC-SD was also chosen because it is the main laboratory of the investigators in charge of this project, and allows for the analyses of other metals and/or interferents of concern in the samples. The addresses of the laboratories are:

SSC-SD, Code 2375,
53475 Strothe Road,
San Diego, CA 92152-6325

Battelle Sequim Operations PNNL,
1529 W. Sequim Bay Rd.,
Sequim, WA 98382
(Battelle's Federal ID number is 31-4379427.)

4. Performance Assessment

4.1 Performance Criteria

The performance of the TCA was assessed from measurements of samples following U.S. EPA accepted methodology. Copper concentrations measured with the TCA were compared with copper measurements done by GFAA at SSC-SD, and by ICP-MS at Battelle. Also, laboratory characterization was performed at SSC-SD, to evaluate some of these criteria. The performance of the TCA in measuring copper concentrations in the effluent were estimated from the similitude among these analyses (Table 5).

Table 5 Performance criteria.

Performance Criteria	Description	Primary or Secondary
Limit of Detection	Minimal total recoverable copper concentration that the TCA is able to measure.	<i>Primary</i>
Working Range of Concentrations	Maximum range of total recoverable copper concentrations that the TCA is able to measure.	<i>Primary</i>
Precision of Measurement	Precision ($\pm 3 \mu\text{g L}^{-1}$) on the measurement of total recoverable copper at $30 \mu\text{g L}^{-1}$ level.	<i>Primary</i>
Factors Affecting TCA Performance	Identification and description of operating conditions and matrix effect on the response of the TCA.	<i>Primary</i>
Reliability of the Measurements	Comparison of measurements of total recoverable copper by TCA, with measurements in discrete samples by ICP-MS and by GFAA.	<i>Primary</i>
Reliability of TCA	The TCA will require maintenance once a month.	<i>Primary</i>
Cost of Operation	The total amount of funding required per year for the operation of the TCA.	<i>Primary</i>
Easy of Use	Description of the number of operators needed, and of skills and training required for the operation of the TCA.	<i>Secondary</i>
Maintenance	Discussion of routine required maintenance, including frequency, labor involved, and level of training required for maintenance personnel.	<i>Secondary</i>

Several criteria were considered important for a successful demonstration. As shown in Table 5, most of the criteria are based on quantitative aspects of the routine measurement of total recoverable copper by the TCA, including sensitivity, precision and accuracy in comparison to analyses of discrete samples under laboratory conditions at Battelle and SSC-SD and at the laboratory characterization. If the agreement between these data is within the performance objectives from Table 2, then the demonstration of the TCA was considered successful.

Different conditions regarding salinity and total recoverable copper concentration were targeted at the demonstration sites. As indicated in sections 2.2 on Previous Testing of Technology and 3.5 Pre-Demonstration Testing and Analysis above, the response of the TCA is affected by the salinity of the effluent. Therefore, the demonstrations were chosen to include a range in the salinity of the effluent, and to include both simple and constant water matrix and a complex mixture of matrices, such as changes in the salinity throughout a demonstration (i.e., rain events in the dry docks). Another consideration for the demonstrations was having either a constant total recoverable copper concentration or a large range of copper concentration in the effluent.

4.2 Performance Confirmation Methods

The results of the demonstration and the effectiveness of the technology were mainly evaluated from the comparison with total recoverable copper measurements at Battelle and SSC-SD. A total of 54 discrete samples were sampled, 18 samples at each demonstration site, 9 samples of these 18 samples in each of the second and the final week of the demonstration. While the TCA measured these concentrations *in situ*, and at near real time, concentrations measured off-site in discrete samples were done at both Battelle and SSC-SD some time after sampling, following state-of-the-art trace metal clean techniques, and U.S. EPA approved analytical methods (U.S. EPA, 1992, 1992a, 1992b, 1996). The demonstration was considered successful when the statistical comparison among the different methods for measuring total recoverable copper showed that their results were not significantly different at the 95% confidence level. Another level of proficiency was evaluated as the precision of the increase in concentration measured for the automatic calibration measurements, where an agreement within $\pm 3 \mu\text{g L}^{-1}$ at the $30 \mu\text{g L}^{-1}$ indicated a successful demonstration. The performance criteria and confirmation methods for the demonstration are shown in Tables 2 and 6.

4.2.1 Demonstration at Puget Sound Naval Shipyard

The TCA had its first industrial demonstration at dry dock 6 of PSNS from 7 July to 22 August 2003. Results from this demonstration indicate that an initial period of about one week is required in order to reach baseline response (Figure 23). This is needed to flush the TCA plumbing system of any internal source of metal in order to measure the single $\mu\text{g L}^{-1}$ copper concentrations in the effluent. The effluent was seawater from cooling of a vessel docked in dry dock 6, and from the adjacent Sinclair Inlet.

Table 6 Performance criteria and confirmation methods for the demonstration of the TCA.

Performance Criteria	Expected Performance (pre demo)	Performance Confirmation Method	Actual (post demo)
PRIMARY CRITERIA (Performance Objectives) (Qualitative)			
Factors Affecting TCA Performance	<i>Salinity effects</i>	<i>Observations from operation of TCA</i>	<i>Yes</i>
PRIMARY CRITERIA (Performance Objectives) (Quantitative)			
Cost	<i><\$3K/yr</i>	<i>Cost calculation</i>	<i>No</i>
Limit of Detection	<i><10 $\mu\text{g L}^{-1}$</i>	<i>Comparison with concentrations in discrete samples measured at Battelle and SSC-SD</i>	<i>Yes</i>
Working Range of Concentrations	<i><10 $\mu\text{g L}^{-1}$ to 50 $\mu\text{g L}^{-1}$</i>	<i>Comparison with concentrations in discrete samples measured at Battelle and SSC-SD</i>	<i>Yes</i>
Precision of Measurement	<i>$\pm 3 \mu\text{g L}^{-1}$ at 30 $\mu\text{g L}^{-1}$ level</i>	<i>Comparison with concentrations in discrete samples measured at Battelle and SSC-SD</i>	<i>Yes</i>
Reliability of the Measurements	<i>$\pm 15\%$ within working range</i>	<i>Comparison with concentrations in discrete samples measured at Battelle and SSC-SD</i>	<i>No</i>
SECONDARY CRITERIA (Performance Objectives) (Qualitative)			
Easy of Use	<i>One week training sufficient for operation.</i>	<i>Experience from demonstration operations</i>	<i>Yes</i>
Maintenance	<i>Once a month</i>	<i>Experience from demonstration operations</i>	<i>No</i>

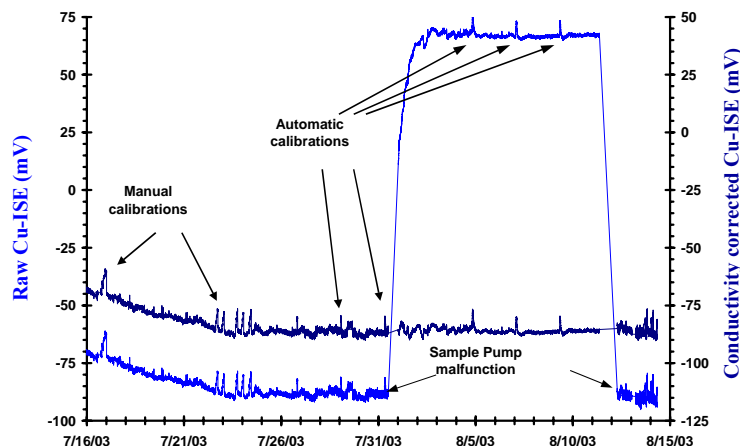


Figure 23 Potential (mV) observed for the Cu-ISE throughout the demonstration at PSNS. The potential in light blue color is uncorrected, and the potential in dark blue color is corrected for both conductivity and for the baseline change due to the malfunction of the sample pump. For clarity the y-axis for the corrected Cu-ISE is offset by 25 mV.

An objective of the demonstration at PSNS was to examine the effects a 30-day maintenance period had on instrument performance. However, during the demonstration there was a malfunction, and this objective was not met. The sample pump failed between the third and fourth week of demonstration (Figure 23), which was identified and fixed sometime in the fourth week.

In spite of the failure of the sample pump, there was continuous, but unregulated, flow of effluent thru the TCA. An effect of the change in flow was a change in the baseline response of the Cu-ISE (Figure 23). This was due to the excessive acidification of the sample, in comparison with normal operation of the TCA. However, once the raw potential measured by the Cu-ISE is corrected for both baseline change and conductivity effects, the response indicates a continuous baseline for the last three weeks of the deployment (dark blue data in Figure 23). Furthermore, a good response of the Cu-ISE to automatic calibrations (i.e., injection of known concentrations of copper to the effluent) was observed.

The concentration range of total recoverable copper measured by the TCA corresponds to that measured by conventional methods. Once the response is corrected for both the change in baseline and the effects of conductivity, the resulting measured total recoverable copper concentrations agree with the range measured at both Battelle and SSC-SD (Figures 24 and 25, Table 7). This range of 3.2 to 7.2 $\mu\text{g L}^{-1}$ (Table 7) was measured as total recoverable copper concentrations in grab samples obtained during the second and fourth week of the demonstration from the effluent of dry dock 6 at PSNS. This range is in the lower limit for the dynamic range of the TCA, and is well below both the concentrations for evaluation of precision of the TCA (i.e., 30 $\mu\text{g L}^{-1}$; Tables 2, 5, and 6) and the NPDES maximum daily limit of 33 $\mu\text{g L}^{-1}$ permitted at PSNS. This lower range in concentration affects the precision of the measurements when it is evaluated from the comparison with the concentrations measured at Battelle and SSC-SD. They

indicated a range of 104 to -39% and 82 to -33% in the differences of these measurements, with an average of $18 \pm 40 \%$ and $14 \pm 36 \%$, respectively (Table 7). However, the more drastic differences in total recoverable copper measured by the TCA to those measured by the other analytical techniques are observed in the initial samples for both grab sample periods. This excess difference could be attributed to the equilibration time required. The initial equilibration time at the beginning of the demonstration could include the first four samples, and another equilibration time could be due to the fixing of the sampling pump, and the increase in flow rate in the TCA. In contrast, statistical comparison using linear regression (Miller and Miller, 1984) indicates that the TCA provides measurements that are not significantly different than those from Battelle and SSC-SD at the 95% confidence level. This is concluded as the calculated 95% confidence limits for the intercept ($a = -2.84 \pm 7.67$ for Battelle; $a = -1.36 \pm 4.25$ for SSC-SD) and for the slope ($b = 1.84 \pm 1.74$ for Battelle; $b = 1.44 \pm 0.92$ for SSC-SD) include the values of zero and one respectively.

The measured concentrations also agree with those expected from the manual and automatic calibrations (Figures 25 and 26). However, three unexplained spike concentrations on the order of $55 \mu\text{g L}^{-1}$, that lasted few minutes, were observed during the demonstration. While the origin of these spikes is unknown, they do not seem related to the effluent, as changes in effluent concentrations seem to last in the order of half a day, they are most probably related to electronic noise in the system and are not included in the data presented in Figure 25.

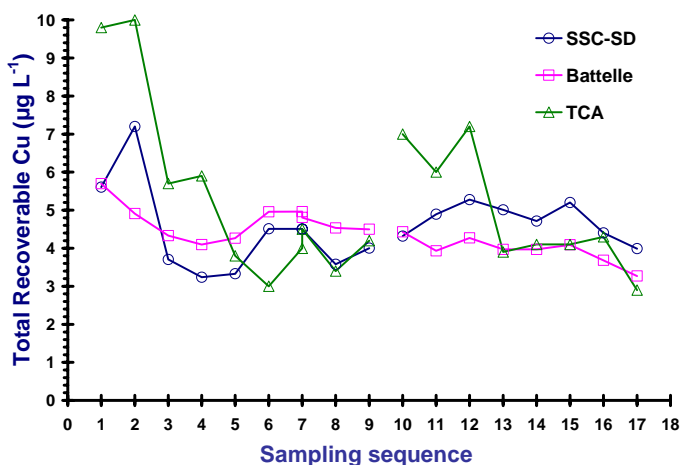


Figure 24 Total recoverable copper concentrations ($\mu\text{g L}^{-1}$) at PSNS measured *in situ* with the TCA and in discrete samples at SSC-SD and at Battelle Marine Sciences Laboratory. The data is from dry dock 6 and is presented as sampling sequence for clarity.

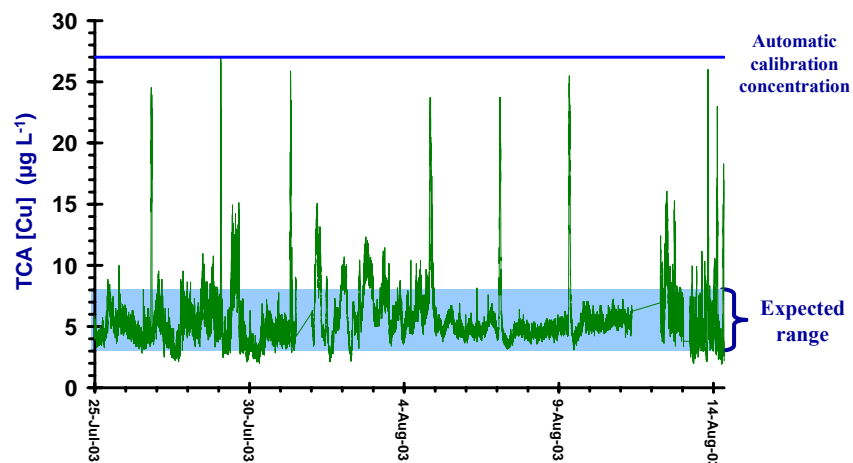


Figure 25 Total recoverable copper concentrations ($\mu\text{g L}^{-1}$) measured by the TCA during the demonstration at dry dock 6 of the PSNS.

Table 7 Comparison of the total recoverable copper concentrations ($[\text{Cu}] \mu\text{g L}^{-1}$) measured in grab samples from PSNS at Battelle and SSC-SD, with those measured in real time, *in situ* by the TCA. The differences are given by subtracting the measured value from that of the TCA.

Date	Time	Battelle [Cu] ($\mu\text{g L}^{-1}$)	SSC-SD [Cu] ($\mu\text{g L}^{-1}$)	TCA [Cu] ($\mu\text{g L}^{-1}$)	Difference Battelle [Cu] ($\mu\text{g L}^{-1}$)	Difference SSC-SD [Cu] ($\mu\text{g L}^{-1}$)	Difference Battelle [Cu] (%)	Difference SSC-SD [Cu] (%)
7/21/03	22:00	5.70	5.6	9.8	4.1	4.2	72	75
7/22/03	6:00	4.91	7.2	10	5.1	2.8	104	39
7/22/03	14:00	4.33	3.7	5.7	1.4	2.0	32	54
7/22/03	22:00	4.10	3.2	5.9	1.8	2.7	44	82
7/23/03	6:00	4.27	3.3	3.8	-0.5	0.5	-11	14
7/23/03	14:00	4.96	4.5	3.0	-2.0	-1.5	-39	-33
7/23/03	22:00	4.96	4.5	4.0	-1.0	-0.5	-19	-11
7/23/03	22:00	4.81	4.5	4.5	-0.3	0.0	-6	0
7/24/03	6:00	4.53	3.6	3.4	-1.1	-0.2	-25	-5
7/24/03	14:00	4.50	4.0	4.2	-0.3	0.2	-7	5
8/12/03	6:00	4.43	4.3	7.0	2.6	2.7	58	62
8/12/03	14:00	3.93	4.9	6.0	2.1	1.1	53	23
8/12/03	22:00	4.27	5.3	7.2	2.9	1.9	69	36
8/13/03	6:00	3.97	5.0	3.9	-0.1	-1.1	-2	-22
8/13/03	14:00	3.97	4.7	4.1	0.1	-0.6	3	-13
8/13/03	14:00	4.09	5.2	4.1	0.0	-1.1	0	-21
8/13/03	22:00	3.68	4.4	4.3	0.6	-0.1	17	-2
8/14/03	6:00	3.27	4.0	2.9	-0.4	-1.1	-11	-27
Average		4.37	4.6	5.2	0.84	0.66	18	14
Standard deviation		0.6	0.9	2.1	1.9	1.7	40	36
Maximum		5.70	7.2	10	5.1	4.2	104	82
Minimum		3.3	3.2	2.9	-2.0	-1.5	-39	-33

The dynamic linearity and precision of the TCA is indicated by the analysis of its response to known additions or spikes of copper. This is done in the case of PSNS as the range in total recoverable copper is low and narrow, and it does not include the $30 \mu\text{g L}^{-1}$ concentration level chosen for the evaluation of precision. Following this criterion, Table 8 shows that the working range of the TCA in industrial situations is at least from 9 to $27 \mu\text{g L}^{-1}$. By taking into consideration the response of the instrument in comparison with measurements by conventional methods the actual working range could be lowered to $4.5 \mu\text{g L}^{-1}$; but this will not provide very precise measurements when compared to the measurements from the two off-site laboratories (Table 7). The precision in Table 8 is evaluated as the percent of the injected copper represented by the standard deviation of the TCA measurements, similar to the calculations for Table 3. Calculated precision for the automatic calibrations indicate a range from 8 to 15% of the expected concentration, with a precision of 8% at the $30 \mu\text{g L}^{-1}$ level. These results are within the expectations for quantitative primary performance criteria of a limit of detection $\leq 10 \mu\text{g L}^{-1}$, a working range of 10 to $50 \mu\text{g L}^{-1}$, a precision of $\pm 10\%$ at the $30 \mu\text{g L}^{-1}$ level, and a reliability of $\pm 15\%$ within the working range (Tables 2, 5, and 6). In comparison, measurements in laboratory conditions indicate a dynamic range for the TCA in DI from $0.5 \mu\text{g L}^{-1}$ to $400 \mu\text{g L}^{-1}$ (Figure 15), and of $2 \mu\text{g L}^{-1}$ to $400 \mu\text{g L}^{-1}$ in artificial seawater (3.2% NaCl in DI; Figure 16), with the response still linear at $400 \mu\text{g L}^{-1}$ in both cases.

Table 8 Average, one standard deviation and precision of the increases of concentration measured for automatic calibrations at PSNS.

Added Total Recoverable copper ($\mu\text{g L}^{-1}$)		TCA Measured Total Recoverable copper ($\mu\text{g L}^{-1}$)		Precision ($\pm\%$)
Average	Standard deviation	Average	Standard deviation	
9.17	0.53	9.2	1.4	15
18.24	0.77	18.0	2.4	13
27.36	1.15	28.2	2.1	8

The measurements by the TCA are related to changes in operational processes at PSNS. The Process Water Collection System appears to have quit at 0700 the morning of 29 July, and the TCA measured an increase in concentration that day (Figure 25). The information provided by the TCA allowed management to determine the effects of this operational change in the effluent of the dry dock.

The TCA has a rapid and accurate response to dynamic spiking. This is illustrated in Figure 26, where the total recoverable copper measured with the TCA through an automatic spike of $20 \mu\text{g L}^{-1}$ to the effluent from dry dock 6 at PSNS indicates a mean increase of $19.7 \mu\text{g L}^{-1}$, from a mean baseline concentration of $4.70 \pm 0.89 \mu\text{g L}^{-1}$ (average \pm one standard deviation) to a mean spike concentration of $24.4 \pm 0.90 \mu\text{g L}^{-1}$. The response time for the TCA was 11 minutes to reach spiked concentrations, and 9 minutes to return to baseline concentration. These results

attest to the precise and rapid response of the TCA under industrial conditions. Furthermore, a result from the demonstration at PSNS was to decrease the ID of the plumbing system within the TCA from ¼" to ⅛" to decrease the response time. And, as shown in Figure 17, the response with the ⅛" ID Teflon® tubing is in the order of 5 minutes.

4.2.2 Demonstration at Pearl Harbor Naval Shipyard

A more pronounced variation in total recoverable copper was observed at dry dock 2 of PHNS, in comparison with dry dock 6 at PSNS. This is indicated by measurements in grab samples by both Battelle and SSC-SD (Figure 27, Table 9), with an observed average of $24.99 \pm 10.99 \mu\text{g L}^{-1}$ and range from 9.85 to $43.70 \mu\text{g L}^{-1}$ for Battelle and an average of $25.3 \pm 9.6 \mu\text{g L}^{-1}$ with a range from 8.5 to $41.3 \mu\text{g L}^{-1}$ for SSC-SD².

As in PSNS, it also took the TCA about a week of deployment to reach equilibrium at the copper concentration in the effluent (Figure 28). After that time, the range in concentrations measured by the TCA corresponds to those determined by both Battelle and SSC-SD. Figure 28 shows the total recoverable copper concentrations measured *in situ* and in real time with the TCA at dry dock 2 PHNS. The range in concentration measured corresponds very well with that measured with other techniques (17.30 to $43.70 \mu\text{g L}^{-1}$; Table 9) and with the range expected for automatic spiking of the effluent (Figure 28). This demonstrates that the dynamic range of the TCA under industrial conditions is at least between 8 to $80 \mu\text{g L}^{-1}$.

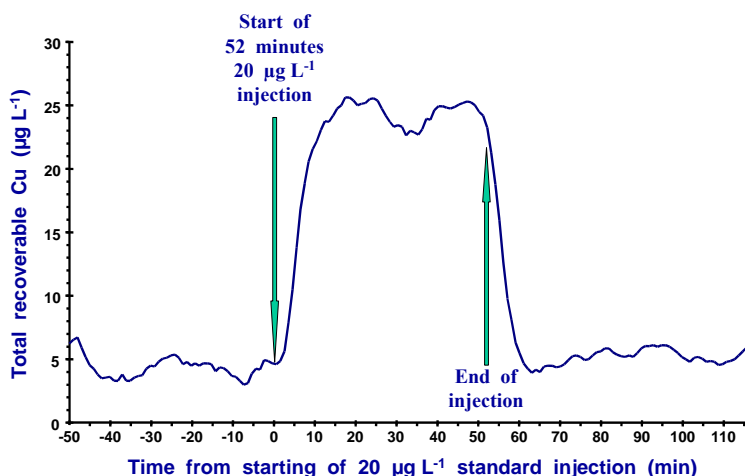


Figure 26 Automatic spiking of $20 \mu\text{g L}^{-1}$ copper, indicating a mean increase in total copper concentration of $19.7 \mu\text{g L}^{-1}$, from a mean baseline concentration of $4.70 \pm 0.89 \mu\text{g L}^{-1}$ (average \pm standard deviation), to a mean spiked concentration of $24.4 \pm 0.90 \mu\text{g L}^{-1}$. The lapse interval to reach this concentration was 11 minutes, with 9 minutes needed to reach baseline concentration at the end of the spiking. Measured on 26 July 2003 at PSNS.

² These statistics are for all of the data for Battelle and SSC-SD and are not included in Table 9.

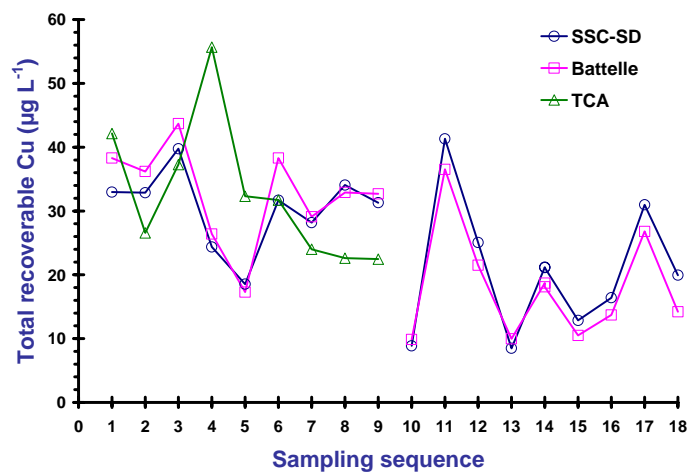


Figure 27 Total recoverable copper concentrations ($\mu\text{g L}^{-1}$) at PHNS measured *in situ* with the TCA and in discrete samples at SSC-SD and at Battelle Marine Sciences Laboratory. The data is from dry dock 2 and is presented as sampling sequence for clarity. TCA sampling stopped during the third week (blocked sampling tube) resulting in no samples taken for sample sequences 10 through 18.

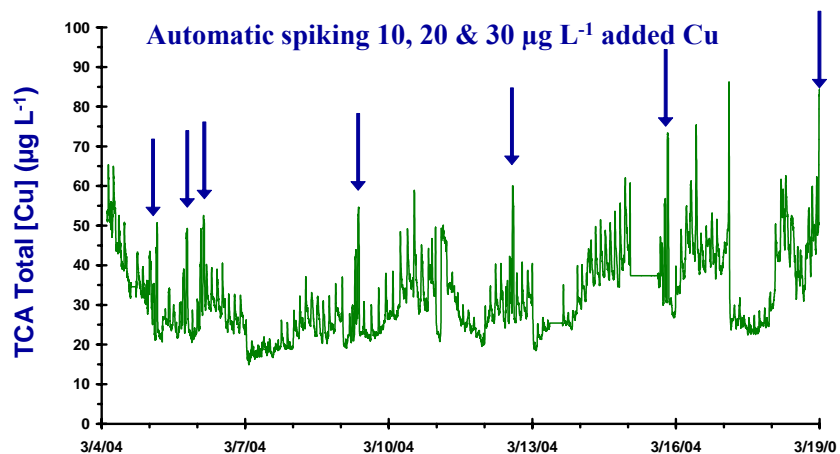


Figure 28 Total recoverable copper and automatic copper spiking of the effluent at dry dock 2 in PHNS.

Table 9 Comparison of the total recoverable copper concentrations ([Cu] $\mu\text{g L}^{-1}$) measured in grab samples from PHNS at Battelle and SSC-SD, with those measured in real time, *in situ* by the TCA. The differences are given by subtracting the measured value from that from the TCA. “NA” is not available. Statistics are for that data with corresponding TCA data only.

Date	Time	Battelle [Cu] ($\mu\text{g L}^{-1}$)	SSC-SD [Cu] ($\mu\text{g L}^{-1}$)	TCA [Cu] ($\mu\text{g L}^{-1}$)	Difference Battelle [Cu] ($\mu\text{g L}^{-1}$)	Difference SSC-SD [Cu] ($\mu\text{g L}^{-1}$)	Difference Battelle [Cu] (%)	Difference SSC-SD [Cu] (%)
3/3/2004	6:30	38.30	33.0	42.1	3.8	9.2	10	28
3/3/2004	14:30	36.20	32.9	26.6	-9.6	-6.3	-27	-19
3/3/2004	22:30	43.70	39.8	37.3	-6.4	-2.5	-15	-6
3/4/2004	6:30	26.40	24.4	55.7	29.3	31.3	111	129
3/4/2004	14:30	17.30	18.5	32.3	15.0	13.8	87	74
3/4/2004	22:30	38.30	31.7	31.7	-6.6	0.0	-17	0
3/5/2004	6:30	29.10	28.2	24.0	-5.1	-4.2	-18	-15
3/5/2004	14:30	32.90	34.1	22.6	-10.3	-11.5	-31	-34
3/5/2004	22:30	32.70	31.3	22.5	-10.2	-8.8	-31	-28
4/5/2004	6:30	9.85	8.9	NA				
4/5/2004	14:30	36.52	41.3	NA				
4/5/2004	22:30	21.50	25.1	NA				
4/6/2004	6:30	9.97	8.5	NA				
4/6/2004	14:30	18.70	21.2	NA				
4/6/2004	14:30	18.10	21.1	NA				
4/6/2004	22:30	10.50	12.9	NA				
4/7/2004	6:30	13.70	16.4	NA				
4/7/2004	14:30	26.80	31.0	NA				
4/7/2004	22:30	14.20	19.9	NA				
Average		32.8	30.4	32.8	-0.02	2.3	8	14
Standard deviation		7.8	6.1	10.9	13.7	13.6	53.5	54.2
Maximum		43.70	39.8	55.7	29.3	31.3	111	129
Minimum		17.30	18.5	22.5	-10.3	-11.5	-31	-34

The evaluation of the precision and dynamic range of the TCA under industrial conditions at PHNS is hindered by the plugging of the sample line ten days prior to the collection of the second set of grab samples. This attests to the requirement of the TCA of daily assessment and inspection in order to correct any obvious problem affecting its response. As explained in section 3.6.2 above, the procedure for the demonstrations included using the first week for installation and equilibration, the second week for calibration and discrete sampling, and the last week for discrete sampling and demobilization. Personnel from SSC-SD were present at the demonstration site for the first two weeks and the final week of the demonstration, with no one assessing the functioning of the TCA in the time in between. Very obvious and easy to resolve problems affected the functioning of the TCA in these times in the three demonstration sites, including malfunctioning of pumps, clogging up or plugging up of sampling tubing by biofouling or particles, and disconnection to the reagents. Simple corrective measures have had allowed for better functioning of the TCA. In the case of the demonstration at PHNS, the plugging of the sample line was corrected by stopping the flow and clearing the line on 4 March 2004; but, the

response of the TCA did not equilibrate for the last week of the demonstration, which is when the last set of grab samples was collected. Therefore, the TCA was not able to measure total recoverable copper concentrations to compare with the grab samples, as indicated by the “Not Available” comment in Table 9.

The TCA measurements are not significantly different than those done by the off-site laboratories. Statistical comparison by linear regression gives a 95% confidence limits for the intercept of $a = 34.98 \pm 42.03$ for Battelle and $a = 43.97 \pm 48.41$ for SSC-SD, and for the slope of $b = -0.068 \pm 1.25$ for Battelle and $b = -0.369 \pm 1.56$ for SSC-SD. The calculated intercept and slope do not differ significantly to the values of zero and one respectively, and the TCA provides measurements that are not significantly different than those from Battelle and SSC-SD at the 95% confidence level at the $30 \mu\text{g L}^{-1}$ copper concentration level observed in PHNS.

The TCA has a precision of $\leq 10\%$ at the $30 \mu\text{g L}^{-1}$ copper concentration level. The precision of the TCA estimated from the increase of concentration measured for the automatic calibrations indicate that the performance criterion for the precision is fulfilled, but the criterion for the reliability was not met. The reliability for 10 and $20 \mu\text{g L}^{-1}$ spikes is above the 15% primary performance criteria (Tables 2, 6 and 10)

Table 10 Average, one standard deviation and precision of the increases of concentration measured for automatic calibrations at PHNS.

Added Total Recoverable copper ($\mu\text{g L}^{-1}$)	TCA Measured Total Recoverable copper ($\mu\text{g L}^{-1}$)		Precision ($\pm\%$)
	Average	Standard deviation	
10	8.4	3.9	39
20	22.0	4.6	23
30	30.8	2.8	9.3

The TCA was able to detect changes in total recoverable copper triggered by industrial operations within the dry dock. In order to keep the water level in the sump in dry dock 2, a regular response is observed coinciding with the timed operation of water pumps, with an 18 minutes operation every two hours. The operation of the pump has an effect on the response of the TCA, which indicates an increase in total recoverable copper every time the pump is activated (Figure 29). This is suspected to be the result of an increase in particulates in the effluent under pumping, and subsequent settling.

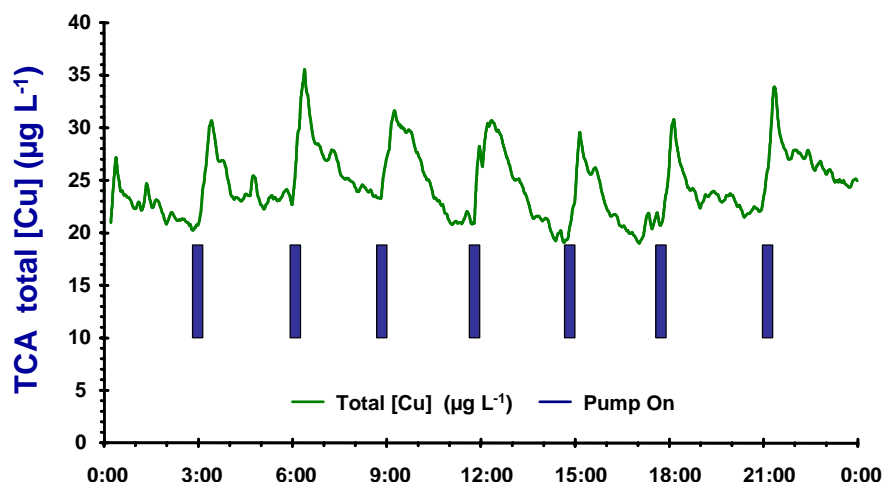


Figure 29 Response of the TCA to pumping in dry dock 2 at PHNS. An increase in total recoverable copper was observed every time the pump was activated, and a subsequent decrease is observed once the pump is deactivated.

4.2.3 Demonstration at Schofield Barracks Waste Water Treatment Plant

For the demonstration at SBWWTP, the TCA was set up in a plastic hut on open ground. The demonstration was done in the summer of 2005 (from 12 July to 24 August), and there were considerable daily fluctuations of temperature in the hut, which affected the TCA (Figure 30). In accordance with the results from Figure 13, no effects for seawater are expected from temperatures above 20°C, and as the range in temperature in the TCA was from 25 to 45°C (Figure 30) no effects were expected here. However, the comparison with the grab samples (Table 11 and Figure 31) shows the TCA measuring a large range in concentrations (3.5 to 33.2 µg L⁻¹) in comparison to the fairly constant concentrations measured in the discrete samples (Battelle: average 5.19 ± 0.47 µg L⁻¹, range 4.32 to 6.06 µg L⁻¹; SSC-SD: 4.4 ± 0.6 µg L⁻¹, 3.4 to 5.6 µg L⁻¹; Table 11). This resulted in having TCA measured concentrations in average $155 \pm 187\%$ (-35 to 584%) and $194 \pm 213\%$ (-14 to 697%) larger than those from Battelle and SSC-SD, respectively (Table 11). This extreme range in concentrations measured by the TCA could be due to the complexity of the treated water, with the presence of organic matter, surfactants, strong organic ligands used in the food industry, residual chlorine, and other compounds of common industrial and household use, that can affect the response of the Cu-ISE.

The effect of temperature is not supported by the correlation between temperature and total recoverable copper measured by the TCA. For the values associated with the grab samples, this correlation has a slope of 0.1 with an r of 0.071. Another interferent present in the effluent is iron; but, total recoverable iron in the grab samples disproved the effect of this interferent (Figure 31). While iron was not completely at steady concentration (32.4 ± 5.9 µg L⁻¹, 24.0 to 45.9 µg L⁻¹), fluctuations in iron concentration do not appear to coincide with those for TCA measured copper concentrations (Figure 31), and regressions of copper measured by the TCA versus iron in grab samples indicate a slope of -0.38 with an r of 0.242, thus disproving the effect of iron alone.

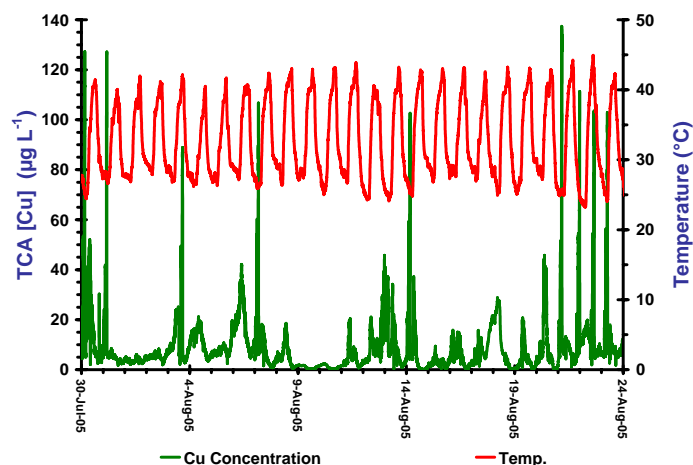


Figure 30 Total recoverable copper, automatic copper spiking measured at the effluent and temperature in the TCA system at SBWWTP.

Table 11 Comparison of the total recoverable copper concentrations ($[Cu]$ $\mu g L^{-1}$) measured in grab samples from SBWWTP at Battelle and SSC-SD, with those measured in real time, *in situ* by the TCA. The differences are given by subtracting the measured value from that from the TCA.

Date	Time	Battelle [Cu] ($\mu g L^{-1}$)	SSC-SD [Cu] ($\mu g L^{-1}$)	TCA [Cu] ($\mu g L^{-1}$)	Difference Battelle [Cu] ($\mu g L^{-1}$)	Difference SSC-SD [Cu] ($\mu g L^{-1}$)	Difference Battelle [Cu] (%)	Difference SSC-SD [Cu] (%)
7/26/2005	22:05	5.43	4.1	3.5	-1.9	-0.6	-35	-14
7/27/2005	7:12	4.99	3.7	8.4	3.4	4.7	69	125
7/27/2005	15:40	4.99	4.1	4.1	-0.9	0.0	-18	1
7/27/2005	21:07	4.82	3.9	3.6	-1.2	-0.3	-25	-7
7/28/2005	8:12	4.32	3.4	16.5	12.1	13.1	281	383
7/28/2005	19:24	4.33	3.8	9.0	4.7	5.2	108	135
7/29/2005	17:47	4.72	4.1	12.9	8.2	8.8	174	212
7/30/2005	9:44	4.85	4.2	33.2	28.3	29.0	584	697
7/30/2005	19:23	5.14	4.7	9.8	4.7	5.1	91	108
8/21/2005	13:40	5.74	4.2	7.3	1.5	3.0	27	71
8/22/2005	9:05	5.79	5.0	15.8	10.0	10.8	173	214
8/22/2005	16:05	6.06	5.6	13.0	7.0	7.4	115	134
8/22/2005	20:25	5.58	5.4	6.4	0.8	1.0	15	20
8/23/2005	8:40	5.65	4.8	13.5	7.9	8.7	139	183
8/23/2005	8:40	5.11	5.0	13.5	8.4	8.5	164	171
8/23/2005	15:20	5.39	5.0	8.0	2.6	3.1	49	62
8/23/2005	20:25	5.25	4.8	6.4	1.1	1.5	22	32
8/24/2005	7:50	5.23	4.7	31.3	26.1	26.6	499	565
8/24/2005	13:50	5.21	4.6	31.9	26.7	27.3	513	591
Average		5.19	4.5	13.1	7.9	8.6	155	194
Standard deviation		0.47	0.6	9.3	9.4	9.3	187	213
Maximum		6.06	5.6	33.2	28.3	29.0	584	697
Minimum		4.32	3.4	3.5	-1.9	-0.6	-35	-14

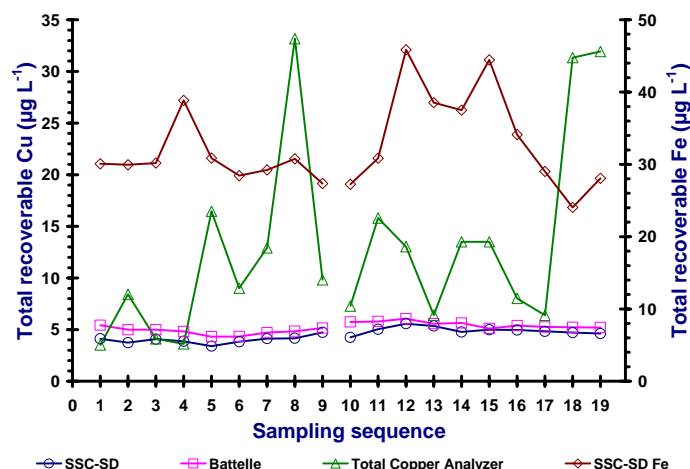


Figure 31 Total recoverable copper and iron concentrations ($\mu\text{g L}^{-1}$) at SBWWTP. Copper was measured *in situ* with the TCA and in discrete samples at SSC-SD and at Battelle Marine Sciences Laboratory. Iron was measured in discrete samples at SSC-SD. The data is presented as sampling sequence for clarity.

The estimated precision of the TCA in SBWWTP is $\pm 20\%$ at the $30 \mu\text{g L}^{-1}$ (Table 12). Increases in copper concentration measured with the TCA during the automatic calibrations show this precision. This precision does not fulfill the quantitative criteria in Tables 2 and 6 of $\pm 10\%$ at $30 \mu\text{g L}^{-1}$, which was fulfilled in PSNS, PHNS, DI and artificial seawater, and the criterion of 15% reliability within the working range of the TCA.

Table 12 Average, one standard deviation and precision of the increases of concentration measured for automatic calibrations at SBWWTP.

Added Total Recoverable copper ($\mu\text{g L}^{-1}$)	TCA Measured Total Recoverable copper ($\mu\text{g L}^{-1}$)		Precision ($\pm\%$)
	Average	Standard deviation	
28.2	20.4	5.6	20
51.2	44.6	5.4	11
74.2	83.3	7.9	11

4.3 Data Analysis, Interpretation and Evaluation

The main advantage of TCA over established procedures is the continuous measurement of the total recoverable copper concentration in the effluent *in situ*. The current approach for measurement of total recoverable copper in effluents is by collecting grab samples, and analyze them in off-site laboratories, with a turnover time of at least a couple of weeks. The logical way to prove the reliability of the TCA is by comparison to concentrations measured in discrete samples by both commercial and research laboratories. Therefore, the dynamic range and

confidence of TCA measurements under industrial situations was evaluated by comparison with measurements in discrete samples analyzed by both Battelle and SSC-SD.

The dynamic range is evaluated by direct comparison of the range in concentrations measured at specific industrial sites; in this case these are the effluents from the dry docks at PSNS and PHNS. The evaluation is based in direct comparison of the ranges in concentration measured by the three options (i.e., TCA, Battelle and SSC-SD). While there was no statistical analysis of the significance of these comparisons, the confidence of the TCA measured values supports these results, and indicates a dynamic range of 8 to 80 $\mu\text{g L}^{-1}$ for the TCA under industrial conditions. In contrast, under controlled laboratory conditions, the response of the TCA was linear in a range from 0.5 to 400 $\mu\text{g L}^{-1}$ in DI, and from 2 to 400 $\mu\text{g L}^{-1}$ in artificial seawater.

The confidence of the total recoverable copper concentrations measured by the TCA was evaluated by correlating them with those measured at each Battelle and SSC-SD. These correlations result in a slope and intercept that are then compared with the perfect correlation values of one and zero, respectively. As it was proved that there is no significant difference between the values measured under industrial conditions and the expected perfect values, then the copper concentrations measured by the TCA are confident at the 95% level.

The precision of the TCA measurements can only be evaluated under controlled conditions. This is due to the large volume of water at constant concentration required for the TCA measurement. The precision was evaluated by performing a series of automatic calibrations in DI under laboratory conditions. For each automatic addition a TCA concentration is used, and the average and standard deviation of all the automatic additions at the same level is evaluated. This evaluation indicates that the TCA has a precision better than $\pm 10\%$ of the expected value at 30 $\mu\text{g L}^{-1}$, this is better than $\pm 3 \mu\text{g L}^{-1}$ at this level.

5. Cost Assessment

5.1 Cost Reporting

The reporting of costs will be done following the Environmental Cost Analysis Methodology (ECAM) developed by the National Defense Center for Environmental Excellence (NDCEE, 1999). However, the ECAM analysis will be done only to level II, as many of the costs that will be incurred for the demonstration and normal operation of the TCA are very difficult to evaluate. Tables 13 and 14 indicate the costs that will be tracked for both the commercial analysis of discrete samples (i.e., the current approach for measurement of total recoverable copper in effluents) and the TCA (i.e., an instrument able to measure total recoverable copper *in situ*, in near real time at DoD relevant concentrations). The calculations used for Tables 13 and 14 are listed in Appendix D.

Table 13 Costs for commercial analysis of discrete samples for total recoverable copper over 10 years at a rate of one sample per day. Costs are in thousands of U.S. dollars.

Direct Environmental Activity Process Costs				Indirect Environmental Activity Costs		Other Costs	
Start-Up		Operation & Maintenance					
Activity	\$K	Activity	\$K	Activity	\$K	Activity	\$K
Initial Contracting	5	Labor to sample discharge	132	Test/analyze waste streams	172		
Sampling equipment purchase including S&H	1	Consumables and supplies	13	Document maintenance	3		
Sampling site preparation	7	Equipment maintenance					
Training of sampling personnel	9						

Table 14 Costs associated with the use of the TCA over a 10 year life span. Costs are in thousands of U.S. dollars.

Direct Environmental Activity Process Costs				Indirect Environmental Activity Costs		Other Costs	
Start-Up		Operation & Maintenance					
Activity	\$K	Activity	\$K	Activity	\$K	Activity	\$K
Equipment purchase	25	Labor to operate TCA	111	Document maintenance	5	Decommissioning	2
Equipment design	10	Utilities	1	Environmental Mgmt. Plan development & maintenance	10	Disposal of hazardous waste	1
Mobilization	2	Mgmt/Treatment of by-products	2				
Site preparation	10	Consumables and supplies	4				
Installation	6	Equipment maintenance	6				
Training of operators	3	Training of operators	2				

5.2 Cost Analysis

Cost Comparison. The alternative activity for the measurement of total recoverable copper in effluents is the commercial analysis of discrete samples. The TCA is not intended to be used in place of discrete samples but be used in situations where continuous control of copper concentrations is required. For this cost analysis we did compare the cost of sampling once per day over a period of 10 years to the TCA's continuous measurement over the same 10 year period. Discrete sampling and off-site analysis results in about \$334,000 for a ten years effort. In comparison, use of the TCA *in situ* to provide continuous measurement of total recoverable copper is calculated to result in an expense of \$198,000 for the same time period of ten years. The cost estimated for operation of the TCA for one year is about \$20,000, which is much more than the expected \$3,000 for performance objectives (Tables 2 and 6). However, the cost of the commercially available TCA is expected to be in the \$25,000 range, assuming a 10 years working life, then \$2,500 would be assigned for yearly cost for the price of the TCA, which accounts for almost all of the \$3,000 predicted.

In comparison to these costs, which are relatively easy to identify and quantify, there are costs that are very difficult to quantify, such as the advantage of having precise information on the concentration of total recoverable copper in near real-time. This type of information can be used

to improve on both best management practices (BMP) as well as on the optimization of the treatment of effluent waters, to the minimum necessary.

Cost Basis. The anticipated costs bases that were used for cost analysis are the costs associated with operation and maintenance of the TCA, and the costs of sampling and analysis by a commercial laboratory (Tables 13 and 14, and Appendix D).

Cost Drivers. The costs of operation and maintenance of the TCA will be driven by the supplies, training and labor needed for these activities. The costs of the current approach of grab samples and off-site analysis are determined by a commercial contract and any internal cost associated with the sampling of the discharge water.

Life Cycle Costs. The costs estimated for the operation and maintenance of a TCA, assuming a lifetime of ten (10) years, are estimated from the demonstration test. These costs will include capital costs, such as purchasing, mobilization and installation cost of the TCA, operation, maintenance and demobilization.

6. Implementation Issues

6.1 Environmental Checklist

The flow rate of effluent that will go throughout the TCA is minimal (i.e., 13.8 mL min⁻¹), and the hazardous characteristics of this analyzed effluent are identical to those from the original effluent. The effluent that will flow throughout the TCA will be returned to the discharge stream. While this safer approach will be undertaken, there are no foreseen potential regulations that may apply to the demonstration.

6.2 Other Regulatory Issues

The application of the TCA for the measurement of total recoverable copper concentrations has not been made known to regulators. However, once the capabilities of the TCA are demonstrated, its use and application will be made available to regulators, and to the public, by means of relevant conferences, and appropriate DoD information centers. The TCA was designed as a process-monitoring instrument, which will help in the optimization of the management of discharges. It is not intended to replace the periodic sampling required under most discharge permits. As such, regulator approval of the TCA is not required.

6.3 End-User Issues

The capacity for real time, *in situ* measurement of total recoverable copper makes commercialization of the TCA an enterprise with great potential for success. The TCA could be used for management in many types of industrial settings, and its potential for reducing and/or eliminating regulatory liability makes it an asset for the industry. Similar concerns are in place in many DoD installations that have to comply with regulatory laws. The potential for the TCA to be a commercialization success is supported by this need.

The characteristics of the effluent are the main factor in using a TCA. As the demonstration at SBWWTP showed, the TCA is prone to erratic response in situation of large temperature variation, and of complex mixture in the effluent. In general, any effluent with excessive organic matter load, with minimal content of bleach, chromium VI, or other oxidizing solution, or with changing concentrations of organic ligands, will not be suitable for total copper measurement by the TCA. However, there is the potential for modification of the TCA for specific effluents. Another reservation for the use of the TCA is that requires daily maintenance/check-up. This is a minimum requirement of checking up the instrument at least once a day for about half-hour, to make sure it is functioning properly.

The TCA used for this demonstration is a custom built prototype. As shown in Figure 1, it consists of three boxes, each about 3×4×1 feet in dimension. The prototype TCA used for this demonstration was designed and built at SSC-SD, and already includes several modifications recommended by Thermo-Orion Inc., the world's largest producer of electrochemical sensors and instrumentations. However, further modifications and downsizing is expected before the TCA is produced commercially by Thermo-Orion. A CRADA is in place for the transferring of the technology to Thermo-Orion.

7. References

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8. Points of Contact

Name, address and role of each point of contact for the demonstration.

POINT OF CONTACT Name	ORGANIZATION Name Address	Role In Project
Ignacio Rivera	SSC-SD Code 23751 53475 Strothe Rd. San Diego, CA 92152-6325	PI
Mike Putnam	SSC-SD Code 2375 53475 Strothe Rd. San Diego, CA 92152-6325	Co-PI
Ernie Arias	SSC-SD Code 2375 53475 Strothe Rd. San Diego, CA 92152-6325	Scientist, Quality Assurance
Daniel Ladd	SSC-SD Code 2373 53475 Strothe Rd. San Diego, CA 92152-6325	Engineering
Bruce Beckwith	Water Program Manager PSNS Code 106.32 1400 Farragut Ave. Bremerton, WA 98314-5001	PSNS Shipyards liaison
John Ornellas	PHNS Code 106.3 667 Safeguard St., Suite 100 Pearl Harbor, HI 96860-5033	PHNS Shipyards liaison
Glenn Atta	PHNS Code 106.3 667 Safeguard St., Suite 100 Pearl Harbor, HI 96860-5033	PHNS Shipyards liaison
Russell Leong	DPW US Army Garrison, Hawaii (APVG-GWV) 572 Santos Dumont Av. Bldg 105, Wheeler Army Airfield Schofield Barracks, HI 96857-5013	SBWWTP liaison

Wayne White	Aqua Engineers, Inc Wheeler Army Airfield, Bldg 345 Airdrome Road Wahiawa, HI 96786	SBWWTP Operations Superintendent
Linda Bingler	Battelle Sequim Operations PNNL, 1529 W. Sequim Bay Rd. Sequim, WA 98382	Commercial laboratory liaison
Steve West,	Head Research and Development, Orion Research, Inc. 500 Cummings Ctr. Beverly, MA 01915	Industry partner

Dated Signature of Project Lead

_____ *Date:* _____

Appendix A: Analytical Methods Supporting the Experimental Design

Method 3020A, Acid Digestion of Aqueous Samples and Extracts for Total Metal Analysis by GFAA Spectroscopy (U.S. EPA, 1992).

<http://www.epa.gov/SW-846/pdfs/3020a.pdf>

Last accessed on 23 March 2006

Method 7211, Copper by Atomic Absorption, Furnace Technique (U.S. EPA, 1992a).

<http://www.epa.gov/SW-846/pdfs/7211.pdf>

Last accessed on 23 March 2006

Method 1640m, Trace Elements in Ambient Water by On-Line Chelation. Inductively Coupled Plasma-Mass Spectrometry (U.S. EPA, 1996).

<http://yosemite.epa.gov/water/owrccatalog.nsf/e673c95b11602f2385256ae1007279fe/c9d46d036acbcfa785256b0600723f6a!OpenDocument>

Last accessed on 23 March 2006

Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels (U.S. EPA, 1996b)

<http://www.brooksrand.com/FileLib/1669.pdf>

Last accessed on 23 March 2006

Appendix B: Data Quality Assurance/Quality Control Plan

B.1. Purpose and Scope of the Plan

The purpose of the Quality Assurance/Quality Control (QA/QC) Plan is to delineate the procedures for monitoring of the demonstration. This is done in order to generate an adequate quantity of high quality data for the validation of the TCA.

B.2 Quality Assurance Responsibilities

It is the responsibility of the quality assurance personnel to monitor the equipment, methods, and records throughout the demonstration and data analysis. They are to ensure the integrity of the data collected. The quality assurance (QA) officer is Mr. Ernie Arias, and he did review the data reduction and validation.

B.3 Data Quality Parameters

There are no quality parameters that could be associated with the measurement of total recoverable copper by the TCA. The instrument provided continuous information on copper concentration in the discharge, which was compared with measurements done by a commercial and a research laboratory on the grab samples. In contrast, the quality of the data generated by these laboratories is affected by the sampling and analytical techniques used; therefore, state of the art trace metal clean techniques were used in sampling and analysis. Sampling was done following U.S. EPA Method 1669 (U.S. EPA, 1996b) on Sampling Ambient Water for Trace Metals, as the use of these techniques assures the representativeness of the samples. Furthermore, the use of trace metal clean techniques in the analysis of the samples provided better accuracy in the measurements.

B.4 Calibration Procedures, Quality Control Checks and Corrective Action

An initial calibration was done on the TCA at the beginning of the demonstration. This calibration was done by injection a copper standard of known concentration at several specific flow rates. In practice this calibration follows the method of standard additions, and was used to set the output of the TCA. The criterion to accept the calibration is a correlation coefficient of 0.95 or better. At SSC-SD the measurement of the copper concentration was done by direct injection of diluted samples into a GFAA spectrometer in accordance with U.S. EPA Method 7211 (1992a). These measurements were done by injections in triplicate for each sample, with relative standard deviation in the absorbance measured of less than 10%. Analysis was done with the method of standard additions, to correct for matrix interferences, with a minimal acceptable correlation coefficient (r) of 0.999 to assure a good precision for the analysis. The Standard Reference Material (SRM) 1643d from the National Institute of Standards & Technology will be included in order to check for the accuracy of the analysis. This SRM will be analyzed every 5 samples, and the analysis will be accepted only when the recovery for this SRM is within $\pm 15\%$ of the certified value. Copper measurements at Battelle will be done by on-line chelation ICP-MS following Method 1640m (U.S. EPA, 1996).

B.5 Demonstration Procedure

The objectives of the demonstration include (i) the evaluation of the precision and accuracy of the TCA to measure total recoverable copper in the effluents in industrial situations, *in situ* and in near real-time, (ii) to demonstrate that the TCA can operate for a month between maintenance visits, and (iii) to find out the cost of operation of the system. These objectives were met by allowing the TCA to measure total recoverable copper at the demonstration sites for a period of time longer than a month. Throughout this time the system was monitored to the minimum necessary, and operation costs were estimated. During each of the second and final weeks of the demonstrations, a total of nine (9) grab samples were collected at each demonstration site. These samples were sent for copper concentration measurements at both the Battelle Laboratory in Sequim, WA, and the analytical laboratory at SSC-SD in San Diego, CA. The collection of samples, blanks, and duplicates, as well as handling and custody control followed U.S. EPA method 1669 (U.S. EPA, 1996b). The correspondence among the copper concentrations measured with the TCA and these two laboratories provides the information needed to determine the reliability, precision and accuracy of the TCA.

B.6 Calculation of Data Quality Indicators

The similitude between the total copper recoverable concentrations measured with the TCA with those measured in grab samples by Battelle and SSC-SD will be evaluated with statistics for the regression line (Miller and Miller, 1984). Regression statistics are calculated using the TCA data as the dependent variable (y), and the Battelle or SSC-SD data as the independent variable (x). Including limits of confidence for the intercept and the slope at the 95% significance level, and a t-test is used to determine if the slope (b) and intercept (a) calculated for the regressions are or are not significantly different than one and zero, respectively. By proving that there is no significant difference between the slope and intercept of this comparison and the values expected for a perfect correlation, then the hypothesis that there is no significant differences at the 95% confidence level between the two analytical methods could be accepted.

The equation for a line or regression of y on x is of the form:

$$y = bx + a$$

The slope (b) and the intercept (a) are calculated with the following equations:

$$b = \frac{\sum_i \{(x_i - \bar{x})(y_i - \bar{y})\}}{\sum_i (x_i - \bar{x})^2}$$
$$a = \bar{y} - b\bar{x}$$

The standard error of the predicted y -value (\hat{y}) of each x ($s_{y/x}$) in the regression is calculated as follows:

$$s_{y/x} = \left\{ \frac{\sum_i (y_i - \hat{y})^2}{n-2} \right\}^{1/2}$$

The standard deviations for the slope (s_b) and for the intercept (s_a) are calculated with the equations:

$$s_b = \frac{s_{y/x}}{\left\{ \sum_i (x_i - \bar{x})^2 \right\}^{1/2}}$$

$$s_a = s_{y/x} \left\{ \frac{\sum_i x_i^2}{n \sum_i (x_i - \bar{x})^2} \right\}^{1/2}$$

The confidence limits for the slope and for the intercept are calculated with the t value for $n-2$ degrees of freedom at a 95% significance level from a t-test table, as follows:

$$b \pm ts_b$$

$$a \pm ts_a$$

In the case where these statistics do include a slope value of one and an intercept value of zero, then it is concluded that there are no significant differences at the 95% for the slope and the intercept to be different to the “ideal” values of one and zero, respectively, and that the two methods provide similar results.

The precision of the TCA measurements was estimated from the automatic calibrations done at each demonstration site. The standard deviation of the increase in copper concentration measured is compared to the spiked concentration. The resulting precision is reported as percent, and indicates both the precision and the reliability of the TCA measurements at each copper concentration level.

B.7 Performance and System Audits

Not applicable.

B.8 Quality Assurance Reports

A final quality assurance report will be submitted as part of the demonstration report.

B.9 ISO 14001

Not applicable.

B.10 Data Format

As the data generated by the TCA, GFAA and ICP-MS are in different specific formats, a tabular form was used to store and work with this data. The tabular form includes data from the three different analytical sources, as well as notes and any ancillary data collected during the demonstration. The tables are presented in Appendix C.

B.11 Data Storage and Archiving Procedures

All the data is stored electronically. Information generated by the TCA is already stored in electronic format. Backup compact disks are used to store this data. At SSC-SD the data from the GFAA is retrieved electronically and stored as Excel files. Data from Battelle will be stored in similar Excel files. All the documentation, records, protocols and reports generated from the demonstration will be retained in archives, and backup storage of all the data generated throughout the demonstration will be done on compact disks.

Appendix C: Laboratory Data

C.1. Total Recoverable Copper measured by Battelle by ICP-MS in discrete samples from PSNS, PHNS and SBWWTP

BATTELLE MARINE SCIENCES LABORATORY
1529 W. Sequim Bay Road
Sequim, WA 98382
(360) 683-4151

9/24/2003

SPAWAR
CONCENTRATIONS OF METALS IN SEAWATER SAMPLES
Samples Received: 7/25/03 and 8/15/03
(concentrations in µg/L - not blank corrected)

(cf#2068)	MSL Code	Rep	Sponsor I.D.	Fe/Pd Cu ICP-MS
SAMPLE RESULTS				
2068*1			PSDD6-07212200	5.70
2068*2			PSDD6-07220600	4.91
2068*3			PSDD6-07221400	4.33
2068*4			PSDD6-07222200	4.10
2068*5			PSDD6-07230600	4.27
2068*6			PSDD6-07231400	4.96
2068*7			Blank	0.186
2068*8			PSDD6-07232200	4.96
2068*9			PSDD6-07232200D	4.81
2068*10			PSDD6-07240600	4.53
2068*11			PSDD6-07241400	4.50
2068*12			PSDD6-08120600	4.43
2068*13			PSDD6-08121400	3.93
2068*14			PSDD6-08122200	4.27
2068*15			PSDD6-08130600	3.97
2068*16			PSDD6-08131400	3.97
2068*17			PSDD6-08131400D	4.09
2068*18			PSDD6-08132200	3.68
2068*19			PSDD6-08140600	3.27
2068*20			Blank	0.135
PROCEDURAL BLANK				0.163
				0.188
METHOD DETECTION LIMIT				
			Fe/Pd	0.04
Project Target Detection Limit				0.05
STANDARD REFERENCE MATERIAL				
CASS-4			Fe/Pd	0.670
CASS-4			Fe/Pd	0.705
CASS-4			certified value	0.592
CASS-4			range	±0.055
			% difference	13%
			% difference	19%
BLANK SPIKE RESULTS				
			Amount Spiked	5.00
			Blank 1	0.614
			Blank 1 + Spike	5.95
			Amount Recovered	5.34
			Percent Recovery	107%
			Amount Spiked	5.00
			Blank 1	0.899
			Blank 1 + Spike	4.64
			Amount Recovered	3.74
			Percent Recovery	75%
MATRIX SPIKE RESULTS				
			Amount Spiked	5.00
			2068*2	4.91
			2068*2 + Spike	10.14
			Amount Recovered	5.23
			Percent Recovery	105%
			Amount Spiked	5.00
			2068*13	3.93
			2068*13 + Spike	8.04
			Amount Recovered	4.11

BATTELLE MARINE SCIENCES LABORATORY
1529 W. Sequim Bay Road
Sequim, WA 98382
(360) 683-4151

SPAWAR, TO0017
CONCENTRATIONS OF COPPER IN SEAWATER SAMPLES
Samples Received: 3/10/04 and 4/10/04
(concentrations in µg/L - not blank corrected)

(cf#2175)		Fe/Pd	
MSL	Sponsor		Cu
Code	Rep I.D.		ICP-MS
SAMPLE RESULTS			
2175*1	PHNSY-03030630		38.3
2175*2	PHNSY-03031430		36.2
2175*3	PHNSY-03032230		43.7
2175*4	PHNSY-03040630		26.4
2175*5	PHNSY-03041430		17.3
2175*6	PHNSY-03042230		38.3
2175*7	PHNSY-03042230D		34.0
2175*8	PHNSY-03050630		29.1
2175*9	PHNSY-03051430		32.9
2175*10	PHNSY-0305BLANK		0.200 b
2175*11	PHNSY-03052230		32.7
2175*12	PHNSY-04050630		9.85
2175*13	PHNSY-04051430		36.5
2175*14	PHNSY-04052230		21.5
2175*15	PHNSY-04060630		9.97
2175*16	PHNSY-04061430		18.7
2175*17	PHNSY-04061430D		18.1
2175*18	PHNSY-04062230		10.5
2175*19	PHNSY-04070630		13.7
2175*20	PHNSY-0407BLANK		0.188 b
2175*21	PHNSY-04071430		26.8
2175*22	PHNSY-04072230		14.2
PROCEDURAL BLANK			0.147 b
			0.220 b
METHOD DETECTION LIMIT			0.04
Project Target Detection Limit			0.05
STANDARD REFERENCE MATERIAL			
1640			89.7
1640			85.4
1640	certified/reference value		85.2
1640	range		±1.2
	% difference		5%
	% difference		0%
CASS-4			0.919
CASS-4			1.41
CASS-4	certified value		0.592
CASS-4	range		±0.055
	% difference		55%
	% difference		137%
CASS-4	Seawater Blank corrected		0.504
CASS-4	Seawater Blank corrected		0.522
CASS-4	certified value		0.592
CASS-4	range		±0.055
	% difference		15%
	% difference		12%
ICV,CCV RESULTS			
ICV			98%
CCV			99%
CCV			98%
ICV			100%
CCV			103%
CCV			98%
BLANK SPIKE RESULTS			
	Amount Spiked		10.0
	Blank		0.520
	Blank + Spike		9.07
	Amount Recovered		8.55
	Percent Recovery		86%
	Amount Spiked		10.0
	Blank		0.892

(cf#2445) (concentrations in µg/L - not blank corrected)

MSL Code	Sponsor Ref ID.	Cu ICP-MS
SAMPLE RESULTS		
2445-1	SB0726052205	5.43
2445-2	SB0727050712	4.99
2445-3	SB0727051540	4.99
2445-4	SB0727052107	4.83
2445-5	SB0727052107D	4.81
2445-6	SB0728050812	4.32
2445-7	SB07280501924	4.33
2445-8	SB0729051747	4.72
2445-9	SB0730050944	4.85
2445-10	SB0730051923	5.14
PROCEDURAL BLANK		0.015 U
METHOD DETECTION LIMIT		0.015
Project Target Detection Limit		0.05
STANDARD REFERENCE MATERIAL		
1640		85.9
1640	certified/reference value	85.2
1640	range	±1.2
	% difference	1%
ICV,CCV RESULTS		
ICV		98%
CCV		100%
CCV		98%
CCV		98%
BLANK SPIKE RESULTS		
Amount Spiked		25.0
Blank		0.015 U
Blank + Spike		26.5
Amount Recovered		26.5
Percent Recovery		106%
MATRIX SPIKE RESULTS		
Amount Spiked		50.0
2445-2		4.99
2445-2 + Spike		52.0
Amount Recovered		47.0
Percent Recovery		94%
REPLICATE RESULTS		
2445-1 1	SB0726052205	5.43
2445-1 2	SB0726052205	5.17
% difference		5%

U = not detected at or above MDL.

BATTELLE MARINE SCIENCES LABORATORY
 1529 W. Sequim Bay Road
 Sequim, WA 98382
 (360) 683-4151

3/28/2006

PAWAR, TO0020
 CONCENTRATIONS OF COPPER IN EFFLUENT SAMPLES
 Samples Received: 9/16/05

(cf#2445)		(concentrations in µg/L - not blank corrected)	
MSL	Sponsor	Cu	
Code	Rep I.D.	ICP-MS	
SAMPLE RESULTS			
2445-11	SBWW-00102	5.74	
2445-12	SBWW-00201	5.79	
2445-13	SBWW-00202	6.06	
2445-14	SBWW-00203	5.58	
2445-15	SBWW-00301	5.65	
2445-16	SBWW-00301 Dup	5.11	
2445-17	SBWW-Blank	0.102	
2445-18	SBWW-00302	5.39	
2445-19	SBWW-00303	5.25	
2445-20	SBWW-00401	5.23	
2445-21	SBWW-00402	5.21	
PROCEDURAL BLANK		0.015 U	
METHOD DETECTION LIMIT		0.015	
Project Target Detection Limit		0.05	
STANDARD REFERENCE MATERIAL			
1640		78.1	
1640	certified/reference value	85.2	
1640	range	±1.2	
	% difference	8%	
ICV,CCV RESULTS			
ICV		101%	
CCV		87%	
CCV		90%	
CCV		87%	
BLANK SPIKE RESULTS			
	Amount Spiked	25.0	
	Blank	0.015 U	
	Blank + Spike	24.2	
	Amount Recovered	24.2	
	Percent Recovery	97%	
MATRIX SPIKE RESULTS			
	Amount Spiked	25.0	
	2445-12	5.79	
	2445-12 + Spike	29.7	
	Amount Recovered	23.9	
	Percent Recovery	96%	
REPLICATE RESULTS			
2445-11	1	SBWW-00102	5.74
2445-11	2	SBWW-00102	5.52
		% difference	4%

U = not detected at or above MDL.

C.2. Total Recoverable Copper measured at SSC-SD by GFAA in discrete samples from PSNS, PHNS and SBWWTP. Total Recoverable Iron measured at SSC-SD by GFAA in discrete samples from SBWWTP.

**Space and Naval Warfare Systems Center
(SSC-SD)**

August 29, 2003

Code 2375
53560 Hull Street
San Diego, CA 92152-5001
(619) 553-2373

Sample ID	Total Recoverable Copper		Duplicates RSD %
	Average [Cu] $\mu\text{g L}^{-1}$	Std. Dev. [Cu] $\mu\text{g L}^{-1}$	
PSDD607212200	5.6	0.75	
PSDD607220600	7.2		
PSDD607221400	3.7		
PSDD607222200	3.2		
PSDD607230600	3.3		
PSDD607231400	4.5		
PSDD607232200	4.5		0.2
PSDD607232200Du	4.5		
PSDD608120600	4.3	0.02	
PSDD608121400	4.9		
PSDD608122200	5.3		
PSDD608130600	5.0		
PSDD608131400	4.7		7.0
PSDD608131400D	5.2		
PSDD608132200	4.4		
PSDD608140600	4.0		
PSDD6071603Blin	5.1		
PSDD607160315pp	19.4		
PSDD607160330pp	32.2		
PSDD6071703Blin	4.3		
PSDD607240600	3.6		
PSDD607241400	4.0		
BLANKS			
PSDD6 Field Blk	0.0051		
PSDD6Blnk081403	0.032		
PSDD6 HNO ₃	0.4		
STANDARDS			
Cu1000PSNS81303	959.7		
Cu1000PSNS81203	891.9		
PSDD6WfrLstCal	4.3		
Cu1000PSNS71703	954.2		
Cu1000PSNS72303	878.9		
STANDARD REFERENCE MATERIAL			Recovery
SRM 1643d			% of
	19.5	1.42	20.5 \pm 3.8
			95
PROCEDURAL BLANK			Limit of Detection
1N QHNO₃			(3 \times standard deviation)
	0.058	0.059	0.176

**Space and Naval Warfare Systems Center
(SSC-SD)**

Code 2375
53560 Hull Street
San Diego, CA 92152-5001
(619) 553-2373

April 19, 2004

Total Recoverable Copper			
Sample ID	Average [Cu] $\mu\text{g L}^{-1}$	Std. Dev. [Cu] $\mu\text{g L}^{-1}$	Duplicates RSD %
PHNSY0303040630	33.0		
PHNSY0303041430	32.9		
PHNSY0303042230	39.8		
PHNSY0304040630	24.4		
PHNSY0304041430	18.5	1.9	
PHNSY0304042230	31.7		
PHNSY0305040630	28.2		
PHNSY0305041430	34.1		
PHNSY0305042230	31.3		
PHNS0405040630	8.9	0.86	
PHNS0405041430	41.3		
PHNS0405042230	25.1		
PHNS0406040630	8.5		
PHNS0406041430	21.2		0.3
PHNS0406041430D	21.1		
PHNS0406042230	12.9		
PHNS0407040630	16.4		
PHNS0407041430	31.0		
PHNS0407042230	19.9		
BLANKS			
PHNSY0305Blank	0.12		
PHNS0407040630B	0.079		
STANDARDS			
1000ppbCu030104	1004		
1000ppbCu030204	896		
PHNSY03020424mS	19.6		
STANDARD REFERENCE MATERIAL		Recovery	
SRM 1643d		% of	
	19.2	0.81	20.5 \pm 3.8
			93
PROCEDURAL BLANK		Limit of Detection	
1N QHNO₃		(3 \times standard deviation)	
	0.027	0.069	0.208
MATRIX SPIKE RESULTS			
		Recovery	
		%	
PHNS0405041430	54.4	119	
PHNS0406042230	24.3	104	

Space and Naval Warfare Systems Center

December 6, 2005

(SSC-SD)

Code 2375

53560 Hull Street

San Diego, CA 92152-5001

(619) 553-2373

Sample ID	Total Recoverable Copper		Duplicates RSD %
	Average [Cu] $\mu\text{g L}^{-1}$	Std. Dev. [Cu] $\mu\text{g L}^{-1}$	
TreatedA 050305	3.9		
TreatedB 050305	4.0		
TreatedC 050305	4.6	0.50	
InfluentA050305	34.0		
InfluentB050303	35.1		
InfluentC050305	35.6		
SB 071305 1455	5.2	0.18	
SB 071405 0905	5.0		
SB 071405 1420	4.8		
SBWW0725051948	5.4	0.12	
SBWW0726050824	4.1		
SBWW0726051446	4.0		6.1
SBWW0726051446D	3.6		
SBWW0726052205	4.1		
SBWW0727050712	3.7		
SBWW0727051540	4.1		
SBWW0727052107	3.9		
SBWW0728050812	3.4		
SBWW0728051924	3.8		
SBWW0729051747	4.1		
SBWW0730050944	4.2		
SBWW0730051923	4.7		
SBWW0821051340	4.2		
SBWW0822050905	5.0		
SBWW0822051605	5.6		
SBWW0822052025	5.4		
SBWW0823050840	4.8		3.1
SBWW0823050840D	5.0		
SBWW0823051520	5.0		
SBWW0823052025	4.8		
SBWW0824050750	4.7		
SBWW0824051350	4.6		
BLANKS			
SBWWTPBIk082305	0.020		
STANDARDS			
SB Cu 4000 ppb	3669		
SBWW0825050800	84.2		
SB STD 073005	3440	43	
SB STD 073105	3596		
SB STD 071405RR	3245		
STANDARD REFERENCE MATERIAL			
SRM 1643d			Recovery
			% of
			20.5 \pm 3.8
	19.2	0.77	94
PROCEDURAL BLANK			
1N QHNO₃			Limit of Detection
			(3 \times standard deviation)
	0.011	0.034	0.101
MATRIX SPIKE RESULTS			
			Recovery
			%
SBWW0726050824	7.5		99
SBWW0727051540	7.4		94
SBWW0730050944	7.5		96
SBWW0822052025	8.8		97
SBWW0824050750	8.4		105
TreatedC 050305	8.3		96
		Average	98
		Std. Dev.	4.0

Space and Naval Warfare Systems Center
(SSC-SD)
Code 2375
53560 Hull Street
San Diego, CA 92152-5001
(619) 553-2373

December 10, 2005

Sample ID	Total Recoverable Copper		Duplicates RSD %
	Average [Fe] $\mu\text{g L}^{-1}$	Std. Dev. [Fe] $\mu\text{g L}^{-1}$	
TreatedA 050305	32		
TreatedB 050305	35		
TreatedC 050305	36		
InfluentA050305	516		
InfluentB050303	401		
InfluentC050305	449		
SB 071305 1455	49	11	
SB 071405 0905	38		
SB 071405 1420	36		
SBWW0713051455	55		
SBWW0714050905	47		
SBWW0714051420	42		
SBWW0725051948	77	5.0	
SBWW0726050824	45		
SBWW0726051446	32		5.2
SBWW0726051446D	30		
SBWW0726052205	30		
SBWW0727050712	30		
SBWW0727051540	30		
SBWW0727052107	39		
SBWW0728050812	31		
SBWW0728051924	28		
SBWW0729051747	29		
SBWW0730050944	31		
SBWW0730051923	27		
SBWW0821051340	27		
SBWW0822050905	31		
SBWW0822051605	46		
SBWW0822052025	39		
SBWW0823050840	37		12.0
SBWW0823050840D	44		
SBWW0823051520	34		
SBWW0823052025	29		
SBWW0824050750	24		
SBWW0824051350	28		
SBWW0825050800	7		
BLANKS			
SBBik0823050840	-0.091		
STANDARDS			
NONE			
STANDARD REFERENCE MATERIAL		Recovery	
SRM 1643d		% of	
	83.7	12.67	91.2 \pm 3.9
			92
PROCEDURAL BLANK		Limit of Detection	
1N QHNO₃		(3 \times standard deviation)	
	0.075	0.312	0.937
MATRIX SPIKE RESULTS		Recovery	
		%	
SB 071405 0905	148		113

Appendix D: Cost Assessment Data

D.1.1 Estimation of commercial analysis of discrete samples for total recoverable copper measurement for a ten years period (Table 13).

- 1) Startup
 - a) Initial Contracting
 - i) Administrative
 $72 \text{ hours @ } \$68.63 \text{ hour}^{-1} = \$4,941.36$
 - b) Sample Equipment Purchasing
Materials $\$982.00$
 - c) Site Preparation
 - i) Mechanical Technician
 $120 \text{ hours @ } \$61.09 \text{ hour}^{-1} = \$7,330.80$
 - ii) Materials
 $\$2,660.00$
 - d) Training of Sampling Personnel
 - i) Chemistry Technician
 $120 \text{ hours @ } \$72.57 \text{ hour}^{-1} = \$8,708.40$
- 2) Operations and Maintenance
 - a) Labor to Sample Discharge
 - i) Chemistry Technician
 $3,650 \text{ sampling events @ } 0.5 \text{ hour event}^{-1} @ \$72.57 \text{ hour}^{-1} = \$132,440.00$
 - b) Consumables
 - i) Materials
 $3,650 \text{ sampling events @ } \$3.50/\text{sample} = \$12,775.00$
- 3) Indirect Environmental Activity Costs
 - a) Test/analyze waste stream
 $3,650 \text{ samples @ } \$47.00 \text{ sample}^{-1} = \$171,550.00$
- 4) Document maintenance
 - a) Administrative
 $10 \text{ years @ } 4 \text{ hours year}^{-1} @ \$68.63 \text{ hour}^{-1} = \$2,745.00$

D.1.2 Estimation of TCA operational costs for a ten years working period (Table 14).

- 1) Startup
 - a) Equipment Purchase
Estimated commercial price \$25,000.00
 - b) Equipment Design
 - i) Engineer
100 hours @ 96.89 hour⁻¹ = \$9,689.00
 - c) Mobilization
Transportation and setup \$2,000.00
 - d) Site Preparation
 - i) Mechanical Technician
120 hours @ \$61.09 hour⁻¹ = \$7,330.80
 - ii) Materials
\$2,660.00
 - e) Installation
 - i) Mechanical Technician
40 hours @ 61.09 hour⁻¹ = \$2,443.60
 - ii) Engineer
20 hours @ 96.89 hour⁻¹ = \$1,937.80
 - iii) Chemist
20 hours @ \$96.89 hour⁻¹ = \$1,937.80
 - f) Training of operators
 - i) Chemistry Technician
20 hours @ \$61.09 hour⁻¹ = \$1,221.80
 - ii) Instructor
20 hours @ \$96.89 hour⁻¹ = \$1,937.80
- 2) Operation & Maintenance
 - a) Labor to Operate TCA
 - i) Chemistry Technician
0.5 hours day⁻¹ × 3650 days @ \$61.09 hour⁻¹ = \$111,489.25
 - b) Utilities
87,600 hours × 0.12 kilowatt-hours @ \$0.1 kilowatts⁻¹ = \$1,051.20
 - c) Mgmt/Treatment of by-products
 - i) Recycling spent consumable containers
2 containers month⁻¹ × 120 months @ \$10 container⁻¹ = \$2,400
 - d) Consumables and supplies
 - i) Reagent replacement
\$36.00 month⁻¹ × 120 months = \$4,320.00
 - e) Equipment Maintenance (5 year interval)
 - i) Pump and tubing replacement \$3,560.00
 - ii) Sensor replacement \$2,100.00
 - f) Training of Operators

- i) Chemical Technician
10 hours @ \$61.09 hour⁻¹ = \$610.90
 - ii) Instructor
10 hours @ \$96.89 hour⁻¹ = \$968.90
- 3) Indirect Environmental Activity Costs
 - a) Document Maintenance
 - i) Administrative
80 hours @ \$68.63 hour⁻¹ = \$5,490.40
 - b) Environmental Management Plan Development and Maintenance
 - i) Administrative
40 hours @ \$68.63 hour⁻¹ = \$2,745.20
 - c) Environmental Specialist
80 hours @ \$96.89 hour⁻¹ = \$7,751.20
- 4) Other Costs
 - a) Decommissioning
 - i) Recycling of electronics
\$600.00
 - b) Disposal of hazardous waste
\$1,200.00